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**The chemical synthesis and crystallisation sequence
of mullite**

Alan Taylor

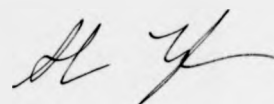
**A thesis submitted for the degree of
Doctor of Philosophy**

**Department of Physics
Warwick University
December 1992**

pour Nicole

Declaration

This thesis is submitted to the University of Warwick in support of my application for admission to the degree of Doctor of Philosophy. It is an account of my work carried out in the Physics Department of the University of Warwick, during the period October 1989 to December 1992 and, except where specifically acknowledged in the text, is a result of my own independent research. No part of this thesis has been submitted in respect of a degree to this or any other university.

A handwritten signature in dark ink, consisting of stylized initials or a name, located in the lower right quadrant of the page.

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...THE BEERS ARE ON ME

Abstract

Mullite stoichiometry powders have been produced using a "water-free" sol-gel approach. The powders are fabricated by mixing aluminium isopropoxide and tetraethyl silicate (TEOS) in butan-1-ol, under conditions where the amount of water allowed into the system from external sources is minimised. The powders are obtained from the solution by rapid removal of the alcohol and other volatile organics. The sols that are produced by the unidentified condensation reactions are then deposited. A homogeneity coefficient has been defined, and is dependant on the crystalline phases that are produced on heating the material to completion of the 980°C exotherm. Two crystalline phases are seen on such a heat treatment, spinel and mullite. This semi-quantitative coefficient is defined as the ratio of the peak height of the x-ray reflections from the (440) plane of spinel and the (331) plane of mullite. Using this definition there is a reproducible and regular variation in the homogeneities of the powders yielded when compared with the length of time the solution was stirred before the sols were deposited. With the concentration used, 0.25M for the isopropoxide and 0.083M for the TEOS, the sols deposited early in the reaction were relatively inhomogeneous. At approximately 19 hours after stirring of both reactants had begun, the homogeneity increased. That is, the amount of mullite that was yielded after completion of the exotherm increased. Continued stirring of the solution gave less homogeneous materials. This behaviour is novel in terms of sol-gel fabrication. The amount of water present in the system, from contamination of the reactants is insignificant compared to the amount of water demanded by the traditional water consuming reactions of sol-gel. Aluminium alkoxides have been found to react directly with alcohols and this reaction has been proposed as being central to the condensation reactions that have been inferred as occurring by the production of Al-O-Si bonds. A phenomenological explanation of the homogeneity has been proposed based on the aluminium alkoxide being the active species after reaction with the alcohol. Linear polymeric species are formed increasing the overall homogeneity of the system, a point is reached in the reaction where the polymers cross-link via aluminium atoms rather than grow in length, the homogeneity of the sols then decreases.

The crystallisation sequence of the materials has been explained in terms of the homogeneity. In particular, the detailed structure of the materials has been related to the coordination of aluminium. At low levels of homogeneity, the material is grossly segregated in terms of the coordination polyhedra of aluminium and silicon. The alumina rich regions have aluminium preferentially in octahedral environments. These materials crystallise to predominantly spinel, an alumina polymorph that probably contains a small amount of silica. Increasing the homogeneity decreases the size of the alumina rich regions. These still exist however due to the stoichiometry of the system. As they decrease in size the interfacial surface area between these regions and the silica rich matrix increases. It is proposed that pentacoordinate aluminium is found in these interfacial areas. The pentacoordinate aluminium is metastable and transforms at 980°C to octahedral and tetrahedral coordinations. It is this transformation that initiates crystallisation of the material. The smaller the volume occupied by the inhomogeneities the more mullite is yielded since the aluminium and silicon are more intimately mixed. Heat treatments of the amorphous material below this temperature will yield spinel from the crystallisation of the unstable alumina rich regions, with some mullite being formed at the interface. Again the smaller the inhomogeneities the more mullite is produced by such a treatment.

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Introduction

Mullite is a material that is currently of considerable interest. Amongst many potential applications technologists are thinking of mullite as a packaging or substrate material for use with electronic devices. Mullite is of interest because of its thermal expansion match to silicon and its low dielectric constant which leads to low electrical losses. It is also thought of as a promising material for structural applications, although due to its relatively low fracture toughness the role it is envisaged that mullite will play is as a matrix material in a Ceramic Matrix Composite (C.M.C.). The reinforcement could be provided by whiskers, fibres or particulates.

The chemical and mechanical stability of mullite in aggressive conditions indicates that this material could be very useful in the type of environment where these conditions exist, combustion engines for example.

Natural deposits of the mineral are rare, but mullite is one of the more commonplace ceramics. It is the product of high temperature reactions involving aluminosilicates, and as such is found in domestic crockery and potteryware. In this form mullite is not particularly useful for the type of applications outlined above. Fabrication of mullite from kaolin type minerals (clays), involves significant contamination problems mainly from metals such as iron and chromium etc. These impurities alter the properties and characteristics of mullite not always in a beneficial way. The stoichiometry of the starting material is rarely the same as the desired end product and so the final material is a mixture of mullite and other phases, usually silica (as a glassy phase or as cristobalite) or alumina (as corundum). The level of control over the stoichiometry and the composition afforded by this fabrication method is thus limited. High temperature routes to make mullite are well known and are the methods used to satisfy most of the commercial demand. These routes involve either the sintering together or the fusion of alumina and silica powders. The high temperatures involved prohibit the fabrication of a C.M.C. using fibres, and significant problems are encountered in attempting to densify when a reinforcing agent is used. This study was initially set up to try to find an alternative route by which to make mullite, a low temperature route that would be amenable to the incorporation of reinforcement agents.

Aims

The initial aims of this project can be formally stated as;

To investigate the fabrication of mullite by chemical, sol - gel, routes with a view to developing a material that may be processed in such a manner as to allow the incorporation of reinforcement agents.

This general objective can be broken down into more specific aims;

The development of a technique for making, via sol - gel routes, a xerogel of mullite stoichiometry.

The identification of the densification conditions required in order to produce a mullite glass of -100% of the theoretical density.

The characterisation of such a glass, including the effect of various processing parameters on the level of homogeneity of the glass and the effect, if any, of the level of homogeneity of the amorphous precursor on the behaviour of the material.

The identification of the conditions required to produce full crystallisation of the glass solely to mullite, or to mullite as the most significant crystalline phase.

The incorporation of silicon carbide, SiC, fibres into the glass.

The identification of the conditions required to yield the maximum density of the composite.

The determination of the effect, if any, of the fibres on the crystallisation sequence of the amorphous precursor.

Chapter 1

Sol-Gel

1.1 Historical Overview

Sol-gel was originally described by Ebelman in 1844 [1]. He observed that the hydrolysis and condensation products of tetraethyl silicate consisted of well defined oligomers, or small polymeric molecules. The solution formed a gel after leaving it exposed to the atmosphere for several weeks. He also noted that leaving the gel to age for a period of months yielded a transparent glass-like material which was hard enough to scratch glass. Later in the nineteenth century this work was followed up by Friedel, Ladenburg and Crafts [2]. Schmidt gives a clear and concise account of the early development of sol-gel [3]. The fundamentals of sol-gel were thus established over a century before they were generally used. In 1929 Konrad *et al* [4] concluded that the role of water is as a reactant and hydrolysis is accompanied by condensation. Sol-gel as a technological process receives its first mention as a patent for dip coatings in 1939 [5]. The amount of attention paid to the field in general however remained small, although important work was done in the 1950s, when Aelion *et al* [6] carried out a systematic survey on the hydrolysis of tetraethyl silicate. Bradley and Mehrotra also carried out work on the chemical properties of metal alkoxides in the 1950s. Bradley [7] in 1950 proposed a theory which correlated the association degree of the alkoxide derivatives with the coordination of the central atom. Mehrotra [8] also worked on the structural aspect of metal alkoxides, specifically the formation of metal oligomers through alkoxy bridges. Work that was specifically aimed at utilising the properties of these chemicals to yield glasses or glass ceramics was not carried out until Dislich in 1971 [9]. The 1970s saw a small but meaningful growth in the amount of work done on both precursor characterisation and the use of metal alkoxides in the fabrication of gels [10]. The decade in which the potential of these systems was really grasped was the 1980s, numerous international conferences were held, the number of publications increased dramatically and sol-gel was generally seen as a viable route to obtain certain glass ceramics. There have been several comprehensive review articles covering sol-gel systems that have been

explored and potential applications of the technology [11,12,13].

Sol-gel has a reputation of being a high-tech synthesis route to obtain materials that are difficult to fabricate by more traditional routes. This reputation may or may not be deserved, however a sol-gel type process occurs naturally in the formation of minerals such as agate and chalcedon. These minerals are produced by the dissolution and precipitation of gels and the formation of the minerals from colloidal silicious acid solutions. Silicious deposits are also responsible for the formation of fossils and petrified wood [14].

1.2 Sol-gel: The chemical synthesis of glasses

Sol-gel is the generic term for the production of glasses by low temperature chemical reactions and heat treatments, as opposed to the high temperature fusions of traditional glass making technologies.

MacKenzie [15] concludes, after comparing gel and melt derived glasses, that for similar compositions the overall structure, and therefore properties, of melt formed and gel derived glasses are similar. Yamane et al have produced a silica glass from sol - gel, with similar properties to commercial silica glass [16]. The high cost of the very pure precursors will prohibit this technique from becoming a standard method for the bulk production of glasses, even allowing for the decrease in price of the precursors as demand increases. The niche that sol-gel derived glasses will probably occupy is in the fabrication of special glasses. The advantages of sol-gel derived materials include higher levels of purity, better homogeneity and new materials. The higher levels of purity stem from the possibility of distilling the precursors [17]. The higher level of homogeneity is due to the gain factor of $10^4 - 10^5$ when mixing scales are considered that is involving molecular species of 0.5 nm compared to the particle sizes of 50 μ m that are commonly used in fusion routes [18]. Schmidt [19] states that sol-gel derived powders, with randomly distributed components are closer to the desired crystalline phase than a mixture of crystallites with the same overall composition but with a much lower degree of mixing. Mukherjee [20] points out that, due to the more uniform cation distribution in gel derived glasses, these materials exhibit markedly different phase separation, nucleation and crystallisation behaviour. The

possibility of new materials stems from two sources, new non-crystalline phases that lie outside the range of normal glass formation due to thermodynamic considerations and, from these materials, the new crystalline phases that may be obtained. With reference to the possibility of new non-crystalline solids, table 1.1 gives several examples of elements that do not form oxide glasses but can be made to form gels.

Element	Oxide glass formation	Gel formation
Si	Excellent	Excellent
Ti	Poor	Excellent
B	Good	Poor
Zr	Poor	Excellent
Al	Reasonable	Good
Ge	Good	Good

Table 1.1 The glass and gel forming ability of various elements (after [21])

There are two separate branches of this technology and these have been compared extensively [22,23,24]; colloidal routes and the so-called alkoxide method. The difference between the two is fundamental, colloids are dispersions of small particles (<500nm) of one material in another [25]. A sol is a distinct class of colloid and is generally taken to mean a suspension of a solid in a liquid in the realms of sol-gel. This branch of the technology is governed by the surface effects of the dispersed colloids, to form a gel the colloids must be destabilised so that the surface charges no longer cause repulsion when a collision between particles occurs. The colloids can then coalesce to give a gel when the translational motion is arrested by particle interactions [26]. The colloids can then form larger particles by a process called Ostwald ripening, where the smaller particles are consumed by the larger ones. The mechanism of growth is of dissolution of the smaller particles and redeposition on the surface of the larger ones. The driving force behind this sequence is the effectively smaller surface energy of the larger particles when the differences in volumes are taken into account.

The second branch of the technology is the alkoxide route. The name of this method is taken from the name of the most common metal oxide precursors; the metal alkoxides.

These chemicals can be reacted with water to give species that will react together forming polymeric macromolecules. The use of the correct starting materials added together in the right order and then heat treated in a manner that will remove all the residual organic compounds, will yield either a powder or a monolithic sample (this also depends on the drying and heating programme). This method then is essentially a method of building up a material on a molecular scale.

Of the two techniques highlighted, the most favoured route in general is the alkoxide method. The reasons for this are the much higher level of mixing of individual molecules at one extreme, compared to colloids that may be hundreds of nanometers in diameter at the other. Although the level of mixing is not important as far as single component systems are concerned, it is vital to the homogeneity of multi-component systems [27]. Densification of materials produced by colloidal routes is dependent on the solubility of the components in the solvent. The sols themselves will frequently have densities approaching the theoretical. Due to Ostwald ripening however, the range of particle sizes that exist will be small, consequently the packing efficiency of these approximately spherical particles will be low. Thus a gel with a large number of pores is produced, reducing the bulk density of the gel.

Gels that are produced by the alkoxide route are thought of as polymeric [12,23,28]. These polymeric species can, in theory at least, be densified to give a monolithic sample with a density approaching the theoretical. The practicalities of densifying these gels however, are such that very convoluted washing, drying and heating procedures are needed.

Despite the problems with shrinkage and cracking upon drying, the polymeric alkoxide route is generally seen as the more versatile and useful of the two routes. For these reasons this route was followed in this study, the nature of the alkoxide precursors only, their reactions with solvents and water, catalysis by acid and base will be reviewed.

1.3 Metal Alkoxides

Metal alkoxides have the general formula,



where M is a metal of valence n, O is oxygen and R is an organic alkyl group, eg. methyl, CH_3 , or ethyl C_2H_5 etc. The chemical and physical properties of these materials are dominated by two factors, the highly polar $M^{\delta+} - O^{\delta-}$ bond, and the size and bulkiness of the alkyl group R. The polarity of the bond varies with the nature of the metal, the bond having an ionic character of approximately 65% for metals such as Al, Ti and Zr. For more

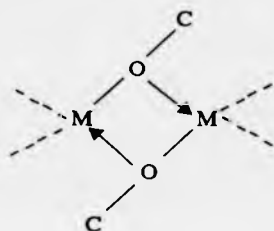


Figure 1.1 Oligomerisation via dative bonds
{after [7]}

electropositive metals such as those found in groups I and II of the periodic table, this ionic character may be as much as 80% [29]. The ability of the metal to increase its coordination number also has an effect in that oligomers may be formed via bidentate dative bonds of the type shown in fig 1.1.

Bradley [7] proposed a structural theory where the metal atoms assume the highest possible coordination number whilst adopting the smallest possible structural unit.

Metal alkoxide	Coordination no. of M	Stereochemistry of M	Minimum degree of association	Observed degree of association
MOR	2	linear	2	
	2	bent	3	
	3	pyramidal	4	4
$M(OR)_2$	6	octahedral	infinite 3-D polymer	
$M(OR)_3$	4	tetrahedral	2	2
	6 and 4	octahedral and tetrahedral	4	4
$M(OR)_4$	6	octahedral	3	3 - 4
$M(OR)_5$	6	octahedral	2	2
$M(OR)_6$	8	cubic	2	2

Table 1.2 Stereochemistry and degree of association of metal alkoxides (after [7 & 30])

Whether oligomers of this type are formed also depends on the steric effects of the alkyl group. Guglielmi and Carturan [31] have collated the degree of oligomerisation exhibited by many metal alkoxides. Mehrotra [30] has published a relationship between the stereochemistry of the metal and the minimum degree of oligomerisation and the degree actually observed. This table is reproduced above in Table 1.2.

The effect of the degree of oligomerisation is seen in the volatility of the alkoxides and also their solubility in organic solvents [18]. The steric effects of the alkyl group affects the degree of association and hence the volatility of the material. This is clearly illustrated by the two most commonly used aluminium alkoxides.

Aluminium *isopropoxide* is a solid at room temperature, Aluminium *secbutoxide* is a liquid. The butoxide group is larger than the propoxide group and hence is sterically more influential, Mehrotra [30] reports that the *isopropoxide* has a degree of association of 4, that is tetrameric, whilst the *secbutoxide* is dimeric.

The bulk of the work carried out in sol-gel research has concentrated on silica and silica based systems. This is because of the glass-forming ability of silica and the desire to densify materials prior to crystallising them, as well as the traditional dominance of silica based compounds in the application of ceramics. However a large number of elements have been studied as fig 1.2. shows.

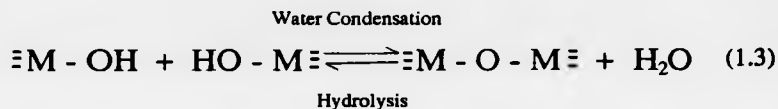
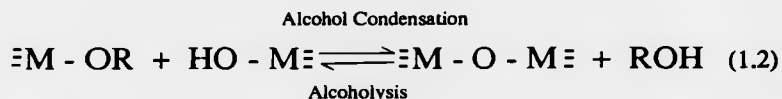
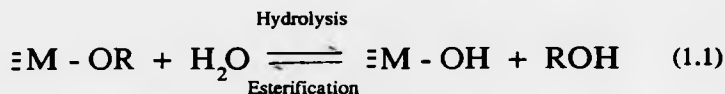
H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac	(Rf)	(Ha)																	

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1.2 The periodic table showing the elements that have been used in sol-gel and/or their alkoxides having been characterised (after [50 & 82]).

1.3.1 Reactions of the Metal Alkoxides.

The metal alkoxides are noted for their reactivity towards water, in fact it is this facet of their character that allows them to be used as the initial building blocks for glasses by sol-gel. The generally accepted and often quoted basic reactions of sol gel are given below by equations 1.1 to 1.4.



Overall



The essence of sol-gel is contained within these chemical reactions. Initially the metal alkoxide is hydrolysed, the hydrolysis products may then go on to react with each other to yield a polymeric species and liberate water. The alternative reaction is for a hydrolysed, or partially hydrolysed species to react with an unreacted precursor with an alcohol being the condensation by-product.

It can be seen that there is an overall consumption of water by the condensation-polymerisation reactions. This leads to the first and most important variables used in the practical fabrication of materials by these chemical methods, the relative amounts of the alkoxide and water used. The molar ratio of water to alkoxide is generally given the symbol R . The amount of water that is actually used can vary enormously, from $R < 0.5$ to $R > 20$ for silicon alkoxides which have a functionality of 4 (that is 4 hydrolysable ligands). The effects of this variation on the final microstructure, and therefore the properties, of the material fabricated are quite marked.

1.3.2 Hydrolysis of Metal Alkoxides

The hydrolysis of silicon alkoxides has been widely studied under a variety of conditions. The mechanisms elucidated for these reactions are generally thought to be applicable to alkoxides of other metals, although the special structural and bonding demands of these other alkoxides must be considered. Since most of the work has been done on the silicon alkoxides, unless specified the following discussion will refer to these compounds alone. There are two boundary conditions for hydrolysis, low and high water concentrations. There are also the effects of catalysts, normally Lowry-Brønsted acids and bases. These four factors are generally seen as pairing up into low water-acid and high water-base. That is the effect of high water and alkaline conditions are seen as having a similar effect, as do low water and an acid environment. The catalysts however accelerate the reactions as would be expected and will be discussed later.

There is some debate as to the mechanisms of hydrolysis under the two boundary conditions. Brinker discusses in detail [32] the reactions that take part in alkoxide sol-gel and critically reviews the mechanisms that are considered likely.

1.3.2.1. The mechanisms of acid catalysis (low water concentrations)

Under these conditions it is generally thought that hydrolysis takes place via a substitution reaction, with an alkoxy group being substituted by an hydroxyl group. The reaction is thought to involve a transition state. The two possibilities for this intermediate are where the silicon atom acquires either a formal positive or negative charge. That is the transition molecule is either a trivalent siliconium ion or is pentacoordinate. The formation of a siliconium ion intermediate was postulated by Swain *et al* [33] as being the rate limiting step in the hydrolysis of triphenylsilyl fluoride. They concluded however that this intermediate state has a less positive charge on the silicon atom than the starting material. This indicates that a pentacoordinate transition state is an easy pathway for the reaction with water. After reviewing these results and the work of Sommer *et al* [34,35], Schmidt *et al* [3] accept that the consensus of opinion was that the siliconium ion did not take part in reactions such as hydrolysis with alkyl- and alkoxysilanes. They however postulate that the siliconium ion would be stabilised by the positive inductive effect of the alkyl radicals for

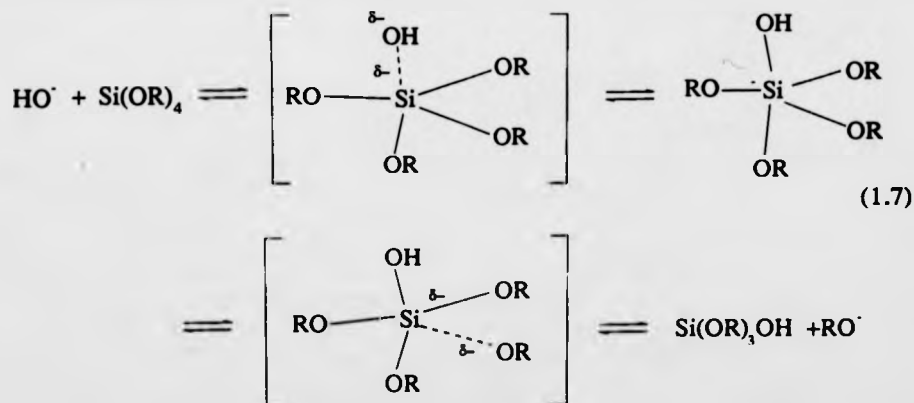
calculations [37] also favour a pentacoordinate transition state, since this will require no activation energy for the removal of water.

Several workers [38 & 39] have proposed hydrolysis mechanisms that do not require tetrahedron inversion. One possible mechanism is shown in eqn. 1.6.

This reaction also involves the protonation of an alkoxy group, a pentacoordinate transition state is not formed however. The silicon acquires more charge as the protonated group withdraws an electron from the silicon. This allows the water to attack the silicon from the side. The alcohol is then released with the oxygen forming a covalent bond to the silicon, whilst withdrawing an electron from one of the hydrogen atoms. This is then released as a proton. Since the silicon acquires more charge in this mechanism than in the S_N2 reaction, electron providing ligands should have more effect, as they will stabilise the silicon during the reaction. Klemperer *et al* [40,41] have investigated hydrolysis using precursors with already established Si-O-Si bonds. They have found that water attacks the Si-OR bond in preference to Si-O-Si bonds. Both types of bonds are attacked when the water / alkoxide ratio is large ($R = 15$), but the alkoxide linkage was the most rapidly attacked. The structural integrity of the precursors was maintained during the initial hydrolysis, this behaviour was also seen by Balfe and Martinez [42] using a dimeric precursor. After longer reaction times it was found this integrity was not kept [40,41].

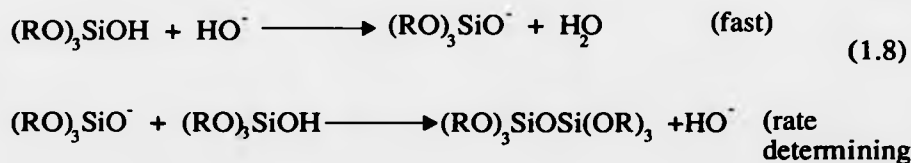
1.3.2.2 The mechanisms of base catalysis (high water concentrations)

Similar to the S_N2 reaction mechanism for acid conditions shown in eqn. 1.5 is the mechanism proposed by Pohl and Osterholtz in eqn. 1.7 where a pentacoordinate transition

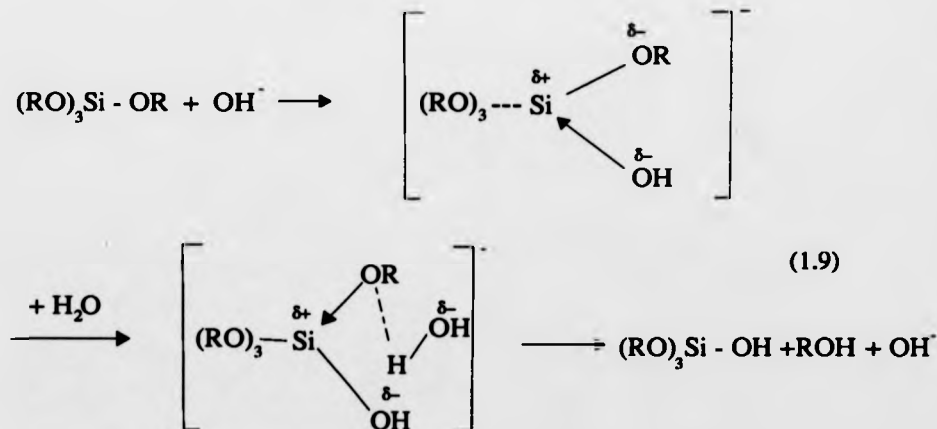


state is involved in the base catalysed reaction. An hydroxyl anion directly attacks the silicon atom resulting in a partial negative charge on the silicon. A redistribution of charge then occurs so that the transition state has a formal negative charge on the silicon. This species then degenerates through a second transition state, where the formal charge on the silicon is changed by one of the alkoxy groups acquiring a partial negative charge. This alkoxy group can then leave the second transition species, the solvent may play a role in the elimination of the ligand. As water is rapidly dissociated under basic conditions the free proton may combine with the negatively charged alkoxy group to give alcohol, the two charged species being stabilised by hydrogen bonding to the solvent prior to their combination. As with the mechanism in eqn. 1.6 this mechanism is sensitive to inductive effects due to the formal charge acquired by the silicon.

Brinker *et al* [43] have suggested a mechanism for a base catalysed nucleophilic attack on silicon leading to a siliconium type intermediate, this is shown in eqn. 1.8.



Schmidt *et al* [44] however favour a pentacoordinated intermediate for basic hydrolysis, this is shown in eqn. 1.9.



1.3.3 Hydrolysis of metal-organic compounds

The term metal-organic has been adopted by Yoldas [17] as a generic term for the alkoxides and alkyl substituted compounds, since organometallic is normally taken to refer to compounds that contain the **M-C** bond. In the case of the Si - C, this is a non-hydrolysable bond and is only broken by oxidation at temperatures in excess of 600°C [45].

The mechanisms of hydrolysis that have been illustrated show that both steric and inductive effects must be taken into consideration. A considerable amount of work has been done on the hydrolysis of silicon compounds. Aelion [6] determined that the hydrolysis rate constant, *H*, the material hydrolysis rate constant, *k*, and the concentration of hydrochloric acid as the solution catalyst were related by;

$$\log H = \log [HCl] + \log k \quad (1.10)$$

It can be clearly seen from table 1.3 that, as the alkyl substituent of the alkoxy group gets larger, the material rate constant rapidly decreases. In agreement with the predictions of the reaction mechanisms the hydrolysis rate is sterically sensitive.

$Si(OR)_4$	$k \times 10^{-2} (l \text{ mol}^{-1} s^{-1} [H^+]^{-1})$
$Si(OCH_3)_4$	19.0
$Si(OC_2H_5)_4$	5.1
$Si(OC_4H_9)_4$	1.9
$Si(OC_6H_{13})_4$	0.83
$Si(O(CH_2)_2CH(CH_2)_3CH(CH_3)CH_2)_4$	0.30

Table 1.3 Material rate constants for the acid hydrolysis of various alkoxysilanes (after [6,32 & 46]).

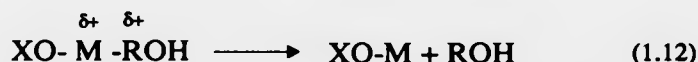
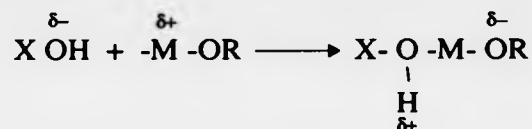
The material rate constant is, as the name suggests, a fundamental property of the species. It takes no account of any other effects such as the solvent in which the hydrolysis was carried out. Chen *et al* [46] hydrolysed various alkoxysilanes in various alcohols and for each silane the hydrolysis rate, *H*, decreased as the alcohol got larger. They qualify these estimated values by pointing out that no account is taken of alcohol exchange

between the silane and the alcoholic medium. Bernards *et al* [47] have also found that the rate of hydrolysis decreases as the ramification of the alkoxy group increases.

Sanchez *et al* [48] have described a general expression for the reaction of metal alkoxides with various other compounds of the form XOH;



Where X can be H for a hydrolysis reaction, M for a condensation reaction or R for an alcohol exchange (or chemical modification as they refer to it). This expression shows the similarity of the various reacting species, These nucleophilic substitutions depend on the charge distribution in the alkoxide and in the transition state, they describe the process in more detail in reaction sequence 1.12.



Blum and Ryan [49] observed no temperature effect on the rate of hydrolysis, this correlates with the statement of Yamane *et al* [50] that catalyst effects far outweigh the role of temperature in hydrolysis.

1.3.4 Alcohol exchange

The process of alcohol exchange is well known although no comprehensive mechanism has to date been proposed. The general reaction is described by eqn. 1.13,

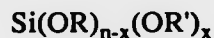


This exchange mechanism is dominated by steric effects, the driving force appears to be for the silane to minimise the steric crowding about the silicon atom, although this is not exclusively the case. Exchange is easier between alcohols and silanes with small alkoxy (or alkyl groups). It is not known whether this exchange takes place between a silane and

an alcohol with identical alkyl groups, nor whether the exchange involves an oxygen atom.

It has been reported by Bernards *et al* [47] that no alcohol exchange is observed when there is no catalyst present, but a significant amount is seen when H^+ is present in the system. When the H^+ concentration was low they found that a lot of exchange had occurred in a $Si(OPr^n)_4 - CH_3OH$ system, whereas very little exchange had occurred in a $Si(OMe)_4 - Pr^nOH$ system. Increasing the concentration of the catalyst however yielded a marked increase in the amount of exchange that had occurred in the methoxide - propanol system. This example illustrates the role of the catalyst in the exchange mechanism, but more importantly it highlights the importance of steric factors in determining the extent of the exchange. This exchange, which is also known as alcoholysis or transesterification, occurs in the order of primary, then secondary then tertiary alcohols, the process is also thought to be an SN_2 reaction [30,31]. As mentioned previously the silane, in general, progresses from a more to a less branched molecule. This may be helped by an increase in the degree of oligomerisation that may subsequently occur. Another example of the role of steric effects is seen with boron alkoxides, these react readily with primary alcohols but not at all with tertiary ones [31]. Increasing ramification of primary alcohols also follows the same reactivity trend, i.e. $MeO > EtO > Pr^nO > BuO$ [18].

The effect this exchange can have on reactions such as hydrolysis and condensation are dependent on the conditions under which the reactions are carried out. The alcohol that is used has been seen to affect the hydrolysis rate of the alkoxide [47,51]. The major effects are, firstly, changing the original silane to give a distribution of silanes of the form;



with the subsequent modification of the material hydrolysis rates. A second effect is the decrease in the concentration of the silanes leading to a corresponding drop in the hydrolysis and condensation rates. If a highly ramified alkoxy group is replaced with a smaller alcohol, the liberated alcohol will have a larger molar volume than the one it is replacing. This will have the effect of increasing the molecular separation between the silanes. This is true whether the reaction chamber is closed or if it is open to allow evaporation, since the larger alcohol is less volatile. The molecular separation does not

appear to have an effect on the rate of hydrolysis, it does affect subsequent condensation though, as the concentration of the partially hydrolysed precursors increases, the time to gelation decreases [52,53] though no difference in the distribution of species is observed in comparison with more dilute solutions [52]. It has also been reported that, in a TEOS - Pr^nOH system under acid and low water conditions, alcohol exchange delays condensation [44].

1.3.5 Hydrolysis products

As the discussion on possible hydrolysis mechanisms indicates, the process of hydrolysis is dependent on the conditions under which the reactions take place,

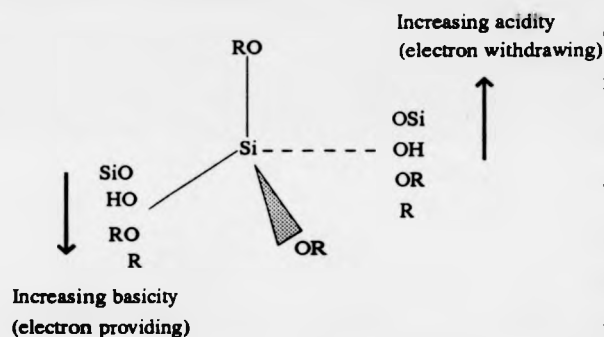


Figure 1.3 The relative acidity of various groups attached to the silicon atom of a metal organic compound (after [32]).

consequently the products of these reactions are different. After the substitution of an alkoxy group for a hydroxyl group has taken place the charge distribution about the silicon is modified compared to that around the unhydrolysed monomer. This has important consequences when the

mechanisms of hydrolysis are taken into consideration. The relative acidity of the various substituents that may be bound to the silicon is shown in fig. 1.3.

When hydrolysis is carried out under acidic conditions the silicon appears to acquire a partial positive charge. The transition state is thus stabilised by basic ligands. The hydrolysis of a monomeric alkoxide species yields initially a monohydroxylated species, $\text{Si}(\text{OR})_3(\text{OH})$. The hydroxyl group is acidic relative to the alkoxy groups, thus the more stable transition states would be achieved by hydrolysis of previously unhydrolysed species. That is, under acidic conditions unreacted monomers are hydrolysed preferentially to those species with one hydroxyl group. These are in turn hydrolysed in preference to those species with two hydroxyl groups attached and so on. This is supported by Raman spectra studies of a TMOS system, where oligomers were hydrolysed more slowly than

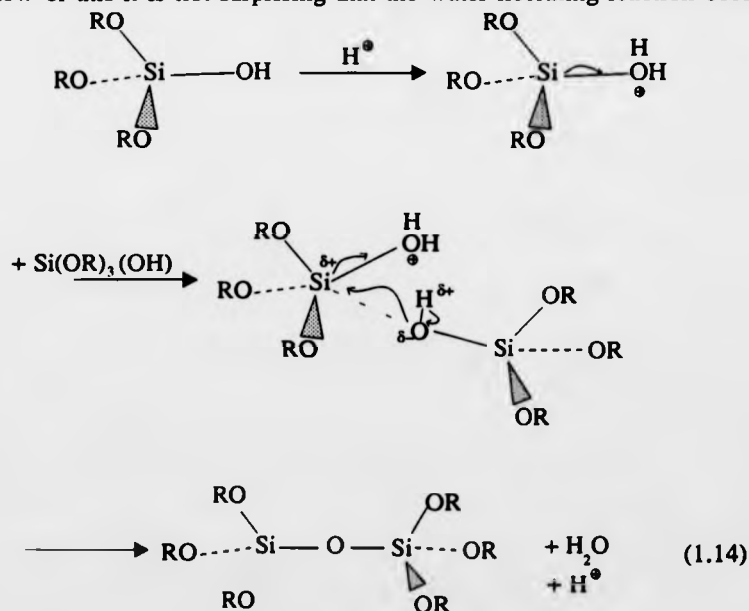
monomers [54].

Under basic conditions the opposite effect is seen. the silicon atom acquires a positive charge, either partial or formal. This is stabilised by acidic ligands, hydrolysis is then more likely to occur to species that have already been partially hydrolysed. This mechanism could in effect be seen as leading to a situation of effective phase separation [12,51,54], where the silanes present fall into the categories of either complete hydrolysis, or little (or even no) hydrolysis.

Under conditions of low pH and high water TEOS behaves in a manner similar to when it is in an basic environment [28].

1.3.6 Condensation

Condensation is a nucleophilic substitution reaction in the same vein as hydrolysis (under acid conditions) and alcohol exchange. The similarities between these reactions are evident from eqns. (5) & (14). The effect of condensation on the charge distribution about a given silicon can be appreciated from fig. 1.3. The basic condensation reactions as given by eqns (2) & (3) indicate that two forms of condensation can take place, one liberating water and the other liberating alcohol, with the reactive group being the hydroxyl group [23,51]. In view of this it is not surprising that the water liberating reaction occurs more



readily than the alcohol liberating one [45], except when the water concentration is very low ($R < 0.5$) then the alcohol liberating condensation becomes significant [55]. The mechanisms of condensation are as hotly debated as those of hydrolysis. The effect of pH plays as crucial a role in condensation as it does in hydrolysis. At low pH the mechanisms of condensation are believed to involve the protonation of the silanol group, one possible mechanism is indicated in eqn. (1.14). The more basic silanols are protonated first, that is monomeric species rather than silanols on a polymeric species. Singly hydrolysed monomers have the most basic silanols and so are expected to be protonated preferentially. Protonation of the silanol increases the acidity of this group and renders the silicon atom more susceptible to attack by a nucleophile.

Under basic conditions the mechanisms of condensation are expected to proceed via penta- or hexacoordinated transition states [32]. Iler [14] has proposed that in aqueous



solution, where the silica is present as silicic acid, a silanol is deprotonated, the remaining oxygen of the silanol then has a formal negative charge and nucleophilically attacks the silicon of another species, this is shown in eqn. 1.15.

As the acidity of the groups attached to the silicon increases, the more the stabilising effect on penta- and hexa coordinated transition states. As is shown by fig. 3 OSi, is a more acidic group than OH which is more acidic than OR. Thus under basic conditions the tendency will be for highly condensed species to form [56].

These mechanisms for condensation are similar to those that occur during hydrolysis and are subject to the same steric and inductive influences, the steric considerations are expected to dominate [32].

1.4 Hydrolysis and Condensation Reaction Rates

The discussion has so far concentrated on the specifics of hydrolysis and condensation. These reactions do not often occur in the separate and isolated manner that is implied by this treatment. For a more complete and correct assessment of the reactions that take place, their relative order, and their effect on the structure of the gel that is formed, it

Factors affecting the final microstructure of the gel

Precursor(s)

pH

Type of catalyst used

Solvent

Water / alkoxide ratio

Addition sequence

Atmosphere above the reaction vessel

In multi-component systems, the relative rates of hydrolysis
of the precursors

Table 1.4 Experimental parameters that can have a direct effect on hydrolysis and condensation reactions.

is useful to list the most important experimental factors that directly influence these effects.

It can be seen from table 1.4 that there are a large number of factors that influence the final structure of the gel. These parameters all, to a certain degree, affect the mechanism and rate of reaction of both hydrolysis and condensation. Their cumulative effect can be summarised however, by the effect they have on the relative rates of the hydrolysis and condensation reactions. The way these reactions relate to each other is possibly the single most important parameter in the fabrication of a material by sol-gel.

There are two extreme situations, where the hydrolysis rate is significantly more rapid than the rate of condensation and where condensation occurs more rapidly than hydrolysis.

The nature of the catalysts employed, either acid or base, will cause different structures to be formed. This is due to their effects on the relative rates of hydrolysis of the precursors present (there may of course be a distribution of precursors due to transesterification) to silanols. The catalysts also affect the rate of condensation of these silanols to silicate polymers and also the subsequent cross-linking of these polymeric units to build up a 3-D network [43].

Under conditions of high pH and/or high water concentration the hydrolysis and condensation reactions are well separated [51,57]. Balfe and Martinez [42] observed with a $\text{Si}(\text{OMe})_4$ solution that at pH9 hydrolysis was very rapid and no unhydrolysed precursor was left after a reaction time of 4 hours. Gelation of this system had occurred however, after a reaction time of 1 hour after adding the base. Hydrolysis was still occurring in this system after gelling had occurred. This type of behaviour was also observed by Kelts *et al* [58], they found that units that had undergone at least one hydrolysis tended to undergo many, that is, at the gel point the high pH systems still had a significant amount of the starting material, approximately 70%. The reason behind this behaviour is the stabilising effect the high pH has on the reaction intermediates, that is those that have undergone a hydrolysis or condensation reaction will be more stable when undergoing a further hydrolysis or condensation reaction. Kelts *et al* [58] also found that, of the species that had undergone some hydrolysis and condensation, approximately 60% of them were tetrasubstituted. Yamane *et al*, studying a silica gel system, found that as the basic catalyst (NH_3) concentration increased a more highly polymerised, but less completely hydrolysed gel resulted [50]. This gives rise to the already mentioned idea of phase separation, giving species that have undergone a significant amount of hydrolysis and species that have undergone little or no hydrolysis. Those hydrolysed can then react together in a water liberating condensation. Those silanes which can condense have many sites available for reaction, thus a highly branched, very cross-linked network is formed. Brinker *et al* [56] found that, in aqueous solution, fully hydrolysed monomers condensed in such a way as to maximise the number of siloxane bonds and to minimise the number of terminal silanols. This may be viewed as a type of particle growth, that is highly condensed sols that are similar to colloids will form in the solution [23,32]. The relatively unreacted monomers will stay in the solution and will continue to react after the sols have reached a size to effectively span the container and cause gelation.

Small Angle X-ray Spectroscopy (SAXS) studies of high pH solutions show that the sols are highly branched and grow with time [12,43,59]. Viscosity measurements also suggest that spherical, or at least highly branched particles are formed, whereas for low pH / low water concentrations weakly cross-linked high aspect ratio polymers are observed by

this method [12,28,60].

According to Mukherjee [20], for high pH solutions the rate of hydrolysis is proportional to the concentrations of the base and the alkoxide. For low pH solutions the rate of hydrolysis is proportional to the concentrations of the acid, the alkoxide and water. In the low pH systems the rate of hydrolysis is less than the rate of condensation and so it is the rate determining step. In agreement with eqn. (10) Bernards *et al* [47] found that the rate of hydrolysis fell with decreasing acid concentration. Kelts *et al* [58] found that at low pH very few tetrahydrolysed species exist. They estimated that, of the polymerised sample, only 26% had undergone reactions at all sites. van Beek *et al* [55] suggest that the species formed at low water concentrations have few residual OH groups. This supports the assertion that under these conditions hydrolysis is the rate determining reaction. When the mechanistic details of hydrolysis and condensation are taken into consideration, a linear growth model would be expected. That is the species that would be preferentially hydrolysed would be unreacted monomers. These would then be available for a condensation reaction. The condensed groups that would be hydrolysed would be those at the chain ends in preference to those in mid-chain. Hence a situation can be envisaged where monomers add together yielding dimers, and these condense together to give long, linear chains with very little cross linking.

Observation early in the reaction, at low water concentrations, have shown that low molecular weight polymers are formed [42,57]. West [37] says that chains are more stable than rings for groupings of < 3-4 tetrahedra or for 10-12 tetrahedra, otherwise rings are the favoured structure. Cross-linking favours rings, with the most stable pathway for condensation being the addition of 4-5 membered rings resulting in structured secondary particles. Other workers have also found that acidic conditions appear to favour the formation of cyclic species [42,55,58,59], Manier *et al* [61] have found that 4 membered rings are stable to water.

The morphology of any gels formed will thus be determined by the relative rates of the hydrolysis and condensation. Yamane *et al* [50] state that base catalysis yields a more highly cross-linked, porous gel than acid catalysis, however it is less completely hydrolysed. As already mentioned the solvent in which the reaction is carried out also has

an effect on the gel structure. The effect of the solvent so far mentioned is in the modification of reaction rates due to transesterification. For example with a constant acid concentration, $\text{Si}(\text{OPr}^n)_4$ showed a minimum gelation time of 6 minutes when methanol was used as the solvent, a time of 16 minutes was recorded when ethanol and n-propanol were used and the time increased to 45 minutes in iso-propanol [47]. Chen *et al* [62] observed that, after acid hydrolysis, the gelation time of TMOS changes from 44 hours in methanol to 152 hours in ethanol, and the times for TEOS to gel in the two solvents were 108 and 242 hours respectively. These examples show that the solvent plays a role in determining the rates of the various reactions. Since the relative rates are also changed the final structure of the gel is also dependent on the solvent. After heat treating their TMOS gels Chen *et al* [62] found that the specific surface area appeared to depend on the solvent. A similar effect was observed by Nakarnish and Soga [63], who studied TMOS, TEOS, and TPOS in their parent alcohols. Gelation occurred in the order given and the pore volume decreased with increasing ramification of the alkoxy group. Quinson *et al* [64] found, whilst studying titanium and zirconium alkoxides in a variety of different solvent types, that, as a general rule, the pore volume of the gel decreased as the polarizability of the ageing solvent decreased.

1.5 Precursor modification

The hydrolysis and subsequent condensation behaviour of a given silane can be altered by the processing parameters mentioned in table 1.4. Another way to control the reactivity of the system is to change the silane that is used, this may involve alkyl substitution of the alkoxy groups [44], the nature of the R group may be changed and chelating ligands may also be employed.

As previously mentioned, alkyl groups can be attached directly to the silicon atom as an Si -C bond which is not hydrolysable. These bonds have a significant effect on the hydrolysis behaviour of the silane. With reference to fig. 1.3, alkyl groups are more basic than alkoxy groups and so will modify the charge distribution about the silicon accordingly. Hydrolysis under acid conditions will be speeded up because of the stabilising effect of the alkyl group on the intermediate state. The final nature of the gel will also be

significantly affected due to the modified silane functionality. As the amount of alkyl substitution increases so does the effect of these groups on the behaviour of the silane. When the precursor has a functionality of 2 the system cannot achieve gelation since an overall connectivity of >2 is required to achieve a 3-D network. van Bommel *et al* [45] found that, for a system of $(1-x)\text{TEOS} \cdot (x)\text{MTES}$, where MTES is $\text{MeSi}(\text{OEt})_3$, the hydrolysis time required to give the minimum gelation time increased as x increases. The minimum gelation time also increases with x . They attributed this behaviour to the faster hydrolysis rate of the alkyl substituted alkoxysilane in the acid step and the reduced condensation rate in the basic step, relative to TEOS. The overall effect of this is a reduced amount of water available to TEOS in both steps. The gelation time also increased as with the ramification of the alkyl substituent and with the amount of substitution. Glaser *et al* [65] formed gels from precursors of different functionality, Fig 1.4 shows a ternary phase diagram of the gel types formed with different ratios of the precursors. A higher

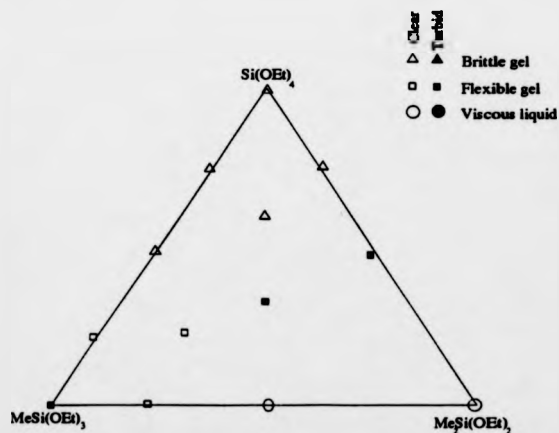


Figure 1.4 ternary phase diagram showing the effect of silane functionality on the resultant gel {after [65]}.

functionality appears to yield a more brittle gel although the gel is clear, a lower functionality also imparts, over specific range, a level of turbidity. In a similar vein Klemperer *et al* [41] also found that gels derived from precursors that contained Si-O-Si bonds were harder, less friable and had smoother surfaces than those derived from monomeric

precursors. Precursors containing more than one silicon are thus another variation available.

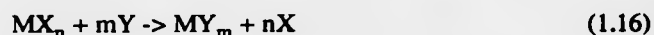
Other forms of substitution can be made to modify the reactivity of the basic alkoxide, these include the replacement of one or more alkoxy groups by an acetate group. Alternatively the nature of the ligand can be changed altogether, for example by substituting a chlorine atom for an alkoxy group. Andrianov [66] shows that the rate of

hydrolysis changes for the examples given above in the order:



1.5.1 Chelating agents

Chelating agents may be added to the system to modify the reactivity of the precursor(s) present. Chelated complexes are more stable than non-chelated ones and so react more slowly. This is of benefit particularly in multi-component systems where the rate of hydrolysis of one precursor is significantly faster than that of another. Typical chelating agents include glycols and organic acids [31]. The chelating reaction is given in eqn. 1.16.



Where m multidentate Y ligands substitute n monodentate X ligands.

The action of the chelating ligand is dependent on the nature of the ligand itself and the coordination geometry it induces about the metal atom. For example $\text{Ti}(\text{OBu}^n)_4$ has been modified with acetic acid to reduce its reactivity with water [53,67]. The acetate groups form bidentate ligands [48], similar to those that are formed when oligomerisation occurs (fig. 1.1), these ligands are not easily removed by water and also increase the steric hindrance to water attempting to attack an alkoxy group. Schmidt [19] says that for $\text{Al}(\text{acac})$ complexes the rate of condensation is slowed down sufficiently that stable homogeneous sols can be formed. The reaction of silicon alkoxides with chelating agents is modified by the inability of silicon to increase its coordination. TEOS has to be refluxed for several hours in the presence of acetic acid for any reaction to occur, and then substitution of an alkoxy group by an acetate group occurs [48]. This will render the silane more reactive towards water, the liberated ethanol can then react with any excess acetic acid to provide an in situ way of forming water. This may be useful in removing the inevitable water concentration gradients that arise when reactant addition is from an external source.

The action of formamide in silica sol-gel is to slow down the hydrolysis rates of the silanes [68,69]. The mechanism behind this is thought to be due to the formamide forming stronger hydrogen bonds with the silanols than they do with the alcoholic medium. A more effective shield about the silanols is therefore formed hindering condensation reactions

[70]. One by-product of the reduction in the rate of hydrolysis is that a more uniform pore structure is formed, this then leads to smaller differential stresses being set up when the gel is dried. Formamide and other chelating agents that have this effect belong to a class of chemicals that are known as Drying Control Chemical Additives (D.C.C.As). This effect on the pore structure allows gels to be dried into monolithic samples.

1.6 Drying and Sintering

The production of a bulk monolithic glass sample directly from a gel has been subject to a considerable amount of investigation [12,24,71] and has been reviewed extensively by Zarzycki [72] and Dislich [13]. Direct conversion of a gel to a monolithic glass sample has been achieved, particularly for silica gels [16,50], but also for other compositions [73]. Production of these bulk samples however involves very careful and intricate drying procedures.

The problems that arise in attempting to produce bulk glasses from gels arise from the very nature of the gels and their synthesis routes. The primary problem facing the production of monolithic glasses from gels is that of cracking. This is due to differential stresses arising from the surface tension acting on pores of various sizes as the solvent is removed. Zarzycki [71] observed that any process that minimised the capillary forces resulting from the surface tension would improve the probability of yielding a monolithic glass directly from the gel. Procedures to yield such monoliths that have been suggested, except for extremely slow drying, include reinforcing the gel, enlarging the pores, reducing the surface tension, making the surface of the gel hydrophobic, hypercritical drying and the use of drying control chemical additives (D.C.C.A.s). The two most intensively studied techniques are hypercritical drying and the use of D.C.C.A.s. Hypercritical drying requires a knowledge of the phase diagram involved so that drying at an appropriate temperature and pressure can be carried out. The liquid phase (predominantly the solvent) is not stable under these conditions and exists as a vapour. As no liquid / vapour interface is present no surface tension or capillary forces are set up. When a gel is being dried, the liquid / vapour interface within the pores sets up stresses due to capillary action. A distribution of pore radii sets up a distribution of these stresses. It is these differential stresses that cause the gel

to fail mechanically. One heat treatment technique which removes the cause of the stresses is autoclaving. In an autoclave the temperature, pressure and nature of the atmosphere about the gel is carefully controlled. Under ideal conditions the atmosphere is manipulated so that the liquid within the pores is vaporised, hence the interface is removed and no capillary stresses are set up. The basic gel network is then left standing free, at this point it is called an aerogel because the fluid filling the pores is a gas. They may in this state be considered rigid but mechanically weak foams. In this state the gel is very fragile and may have a bulk density as low as 5% of the theoretical. Gels of this kind may have applications however, since when left standing in air most of the gel will be air, therefore the dielectric properties will be very favourable in electronic circuit packaging and thermal insulating terms.

The primary benefit of D.C.C.A.s is that they minimise the distribution of pore sizes and increase the average size of pore created by the fabrication procedure [69]. Due to the narrow pore size range, the differential stresses set up on drying are minimised.

A powder with little or no trapped solvent still has alkoxy groups associated with the network, and will shrink upon calcination. Brinker and Scherer [12] have indicated that at least four mechanisms are involved in the shrinking and densification of the network up to and during the gel to glass transition in polymeric gels;

- | | | |
|-----|----------------------|---|
| I | Very low temperature | - Shrinkage due to capillary contraction |
| II | Low temperature | - Condensation polymerisation via the removal of hydroxyl and alkoxy groups, increasing the number of cross links between the chains. |
| III | Near T_g | - Structural relaxation decreasing the amount of free volume, therefore decreasing the free energy of the network. |
| IV | Above T_g | - Viscous sintering where material transport helps form the final dense solid. |

Step I is the most important for the direct production of monoliths, since it is this stage where the gel begins to fracture and fragment if care is not taken. Step II is

alternatively called syneresis and is a continuation of the condensation step, that is the removal of alkoxy and hydroxy groups from the polymeric backbone. The removal of these groups is followed by an increase in the degree of cross-linking between the chains. Some workers [3] believe that, at the slightly elevated temperatures of this step direct condensation between two alkoxy groups can occur with the liberation of an ether.

The final stage in the production of the xerogel is the removal of all the residual organic groups that are trapped in the skeleton of the network. The temperature for the removal of all residues depends on the initial processing conditions, the composition of the material and the exact specification of the heating schedule used. The shrinkage that accompanies the removal of the residual organics can be of the order of 50% or more in terms of a linear dimension and the weight loss may also approach this order of magnitude. The heat treatment schedules that need to be devised to remove the organics, to cause densification and to remove residual hydroxyls are very complex.

There exist many quantitative models to explain the phenomenology of drying [10,12,23,74]. These models relate mainly to the slow removal of solvents from a fluidics standpoint and deal with the resulting stresses set up as a consequence. Upon production of a xerogel, after due consideration to the densification of the skeleton, the fabrication of a monolithic glass sample is produced by mechanism IV of Brinker and Scherer. If the xerogel is a powder this mechanism is improved by pressing.

1.7 Sol - gel synthesis of mullite.

The discussion so far has been limited to essentially single component systems, most useful materials are multi-component. The alkoxide precursors for such a system may not react in the same manner or at the same rate. Silicon and aluminium alkoxides for example, react with water at very different rates, they also form very different products. Silicon alkoxides rapidly build up a 3-dimensional network structure under most conditions, aluminium alkoxides rapidly hydrolyse to give either the hydroxide or oxyhydroxide [75]. This raises the problem of preferential hydrolysis, if water is introduced too rapidly to the alkoxide mixture the more reactive alkoxide will hydrolyse preferentially. The products of this reaction will then condense together leading to the formation of regions within the gel

that are rich in the faster reacting precursor. Hence the overall homogeneity of the gel is diminished. Yamane *etal* [76] conclude from their studies on TiO_2 - SiO_2 systems that the closer the hydrolysis rates of the precursors the higher the level of homogeneity of the gel.

Many methods have been suggested to prevent the preferential hydrolysis of the aluminum precursor in the fabrication of aluminosilicates by sol - gel. These methods include the prehydrolysis of the silicon alkoxide [26,77] and the use of less reactive precursors such as aluminium nitrate [78 - 86]. Some workers have used both of these approaches at once [85,86]. To circumvent the problem of more than one rate of hydrolysis some workers have used a silicon aluminum ester [86,87] as the precursor.

The use of aluminium nitrate, usually in the nonohydrate form, is a technique of introducing water into the reaction system *in situ*, thus avoiding any water concentration gradients that are inevitable when water is introduced from an external source. The prehydrolysis of the less reactive precursor unfortunately also tends to lower the overall homogeneity of the system [43,77]. This is because the hydrolysis and condensation steps cannot be considered separate and discrete, and the formation of any partially hydrolysed species is likely to lead to self-polymerisation.

Mullite has been produced by many workers in the field of sol - gel [21,68,78-84,88-97]. Some researchers have used the method of colloid destabilisation, to yield a gel with the overall mullite composition [21,80,81,84,92-95], others have attempted to obtain a higher level of homogeneity by producing polymeric gels via alkoxide based techniques [68,78-84,88-91,93,96,97]. In alkoxide based mullite sol - gel, the homogeneity of the final gel is dependent on reducing the difference in the hydrolysis rates of the precursors.

1.8 Summary

The technique of making glasses and glass ceramics by sol-gel methods offers several advantages over traditional fabrication methods, these are primarily concerned with the new materials that sol-gel can produce, and the ability to give structural variation without compositional change. The preparation of bulk samples from sol-gel techniques is hampered by several factors, rendering the technique unfavourable against other methods

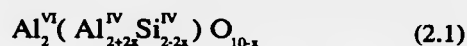
of preparation for more common materials. Within the general field of glass fabrication sol-gel has an important role to play, this role is complementary to traditional techniques and is limited by the small volume of material that can be prepared by these chemical methods. The production of a monolithic sample with a high degree of dimensional control is beyond the present day technology of sol-gel. Films, which are by definition almost two dimensional, suggest a direction of application in which sol-gel may be ideally suited to fill. The large surface area to volume ratio allows a pathway for the controlled removal of residual compounds. This pathway has been the major technological use of sol-gel so far and large scale coatings have been made [98], in fact the all glass façade of the the European Patent Office was coated with a reflective layer by sol-gel [13].

Chapter 2

Mullite

2.1 Occurrence, structure and properties

The only sizable natural deposit of mullite is found on the Isle of Mull, off the west coast of Scotland, and it is from here that the name of the mineral is derived. Commercially mullite is made by two high temperature routes, sintering and fusion. In these processes alumina and silica powders are heated together, at -1700°C for sintering and at temperatures in excess of 1900°C for fusion. Mullite is also formed when kaolin type minerals are heated above -1250°C , the material that results has a nominal composition of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Another way of presenting the composition of mullite is shown in eqn. (2.1).



Where Al^{VI} and Al^{IV} are octahedral and tetrahedrally coordinated aluminium respectively, and Si^{IV} is tetrahedral silicon. The relationship between the aluminium and silicon tetrahedra in aluminosilicates becomes clearer when viewed in this way. It is also obvious that a range of compositions are possible, depending on the quantity of oxygen vacancies in the structure. Within the system $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ there is considerable debate on three specific points. What is the melting behaviour of mullite, i.e. does mullite melt congruently or incongruently? What is the exact location and the range of the region of immiscibility? The final issue is the question of the range of solid solution of mullite.

Concerning the location and range of the region of immiscibility, Takamori and Roy [99] concluded from rapid quenching studies that this region extended from approximately 10 mol% Al to 50 mol% Al, with it existing to about 1650°C . Risbud and Pask [100] conclude from their thermodynamic calculations that the immiscibility region is not quite this extensive, but still exists almost entirely in the silica rich half of the phase diagram. This clearly places the immiscibility region outside the boundaries of mullite. The melting behaviour of a mullite sample is also outside the range of this study, the structure and range of mullite however need to be dealt with in some detail.

2.1.1 Crystal Structure

As already mentioned mullite is thought of as a solid solution of alumina and silica. Mullite is the only thermodynamically stable aluminosilicate at room temperature and atmospheric pressure. The structure of hypothetical 'perfect' stoichiometric mullite is presented in figure 2.1.

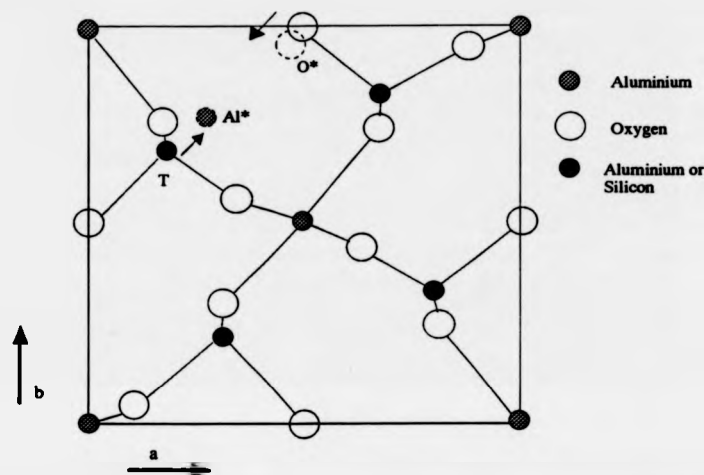
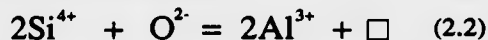


Figure 2.1 Crystal structure of mullite along the (001) plane, the sites with dashed outlines have partial occupancy as the number of oxygen defects increases (after [34 & 35]).

The unit cell is orthorhombic with a slightly longer b_0 than a_0 cell parameter. Chains of octahedral AlO_6 run parallel to the c -axis and are cross-linked by tetrahedral $(\text{AlSi})\text{O}_4$ chains. Open, relatively wide channels run between the octahedral chains along the c -axis [34,101,102]. When only crystallographic considerations are taken into account this range can extend from $x=0$ (sillimanite) to $x=1$ (alumina). The form of alumina that exists at $x=1$ is usually thought to be iota alumina ($i\text{-Al}_2\text{O}_3$) [35,89,102]. The defect structures that are formed with varying x are based on the exchange



The number of vacancies increases by the removal of the bridging oxygens in the cross-linking tetrahedra, O^* . The positions of the tetrahedral cations are rearranged, as the Al/Si ratio increases, with the tetrahedral aluminium taking up Al^* environments. These are available only for aluminium, unlike the bridging T tetrahedra where both aluminium and silicon can occupy the cationic site [35,101].

Although the range of solid solution has the potential to exist over half the phase diagram (at $x=0$ sillimanite is the metastable polymorph with the composition $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), mullite actually only exists over a portion of it. The most general agreement is that the range of mullite exists from $x=0.25$ (composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) to $x=0.4$ ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) [34,89,101,103,104]. Some workers believe that this exaggerates the range, Aramaki and Roy [103] believe that 60 - 63 mol% Al_2O_3 is the range, with a further region of metastability at 67 mol% Al_2O_3 . Al-Jarsha *et al* [89] also believe that aluminous mullites are metastable. Others believe that the range indicated above is too narrow, Colomban and Mazerolles [105] think that the silica rich boundary extends to $x=0.2$. Cameron [104] and Aksay *et al* [35] suggest that $x=0.19$ to $x=0.59$ (57.5 - 76 mol% Al_2O_3) is the region over which mullite forms. This is similar to Schneider and Rymon-Lipinsky [106] who argue that the range mullite occupies is from 58 - 77 mol% Al_2O_3 , with the remainder of the possible solid solution range, on both alumina poor and alumina rich sides being occupied by miscibility gaps.

2.1.2 Properties

Mullite is a material that is currently of considerable interest and many research groups around the world are looking into its synthesis. As already mentioned conventional methods involve high temperature reactions, either solid state or fusion. Chemical fabrication routes are also being investigated and the synthesis of mullite by sol - gel is receiving a lot of attention since it promises a relatively low temperature route to yield a high density monolithic sample.

Mullite is thought of as a useful (or potentially useful) material not because it is strong, but because it retains a lot of its strength at high temperatures. It can be seen from table 2.1 that, while mullite has a flexural strength at room temperature of 270 - 400 MPa, other common ceramics that are of interest as matrix materials such as silicon carbides or silicon nitrides are generally stronger and can have strengths of the order 310 - 655 MPa and 485 - 690 MPa respectively [107]. Mullite does not, unlike zirconia, undergo a destructive phase transition and so can be subjected to repeated thermal cycling without the addition of stabilising compounds which may affect other properties. Apart from its

resistance to creep, mullite is also chemically robust and is not readily attacked by corrosive substances. Mullite is hence a high quality refractory material, but without the strength to make it exceptional. The need to strengthen mullite by reinforcement agents such as particulates, whiskers or fibres is clear. Silicon carbide fibres are the most widely used fibres at present, however the fibres that are currently available are not robust enough to withstand being pressed with a crystalline particulate matrix as this physically damages them. They are also prone to high temperature degradation and so the temperature at which hot pressing is carried out is limited.

Many authors have developed methods and routes to obtain dense monolithic samples of mullite from sol - gel derived powders. These authors have found it necessary to consolidate the powders at high temperatures, $>1300^{\circ}\text{C}$ to achieve a high density. Even with sol - gel derived materials, there has been no reported case (to the author's knowledge) of a highly dense monolith being prepared at low temperatures. Table 2.1 gives a review of the properties and methods of fabrication of various mullite samples.

Table 2.1
Comparison of the properties of dense mullites, produced by various methods.

Reference	[90]	[93]	[93]	[79]	[108]	[35]
Density (%)	> 99	> 99	97.5	95.0		
Consolidation Conditions	1500°C (30 mins) (34 MPa)	1600°C (1hr) (10MPa)	1650°C (3hrs)	1650°C (4hrs) (200MPa)	1400°C (2 tons/cm ²)	
Flexural Strength (MPa)	268 (25°C)	412 (25°C) 416 (1200°C)	364 (25°C) 390 (1200°C)	360 (25°C) >320 (1400°C)	330 (25°C) 450 (1000°C) 300 (1300°C)	200 - 500
Thermal Expansion ($\times 10^{-6} \text{ K}^{-1}$)	5.6	5.1	5.06		4.43 #	4.0
Range (°C)	25 - 1500	20 - 800	20 - 800		20 - 400	20 - 200
Young's Modulus (Pa)	220 $\times 10^9$					
K_{IC} (Pa.m ^{1/2})		2.02	2.13	2.8		2.2
Dielectric Constant					7.1 ± 0.2 (at 1MHz)	6.7

The samples were all prepared from sol - gel derived powders except for ref [35] which quotes review values for the various properties. Ref [79] was prepared from a pyrolysed sol - gel powder. Ref [108] refers to samples containing MgO as a sintering aid, the standard being 0.3 wt%, except for the thermal expansion sample which contained 0.75 wt% MgO.

2.2 Crystallisation sequences

Figure 2.2 shows a flow diagram of the events that occur in aluminosilicates, nominally close to mullite stoichiometry, upon heating. These events raise many questions which will be dealt with subsequently, however, it is useful to summarise these questions before we deal with the observations that have been made and the current wisdom about these events.

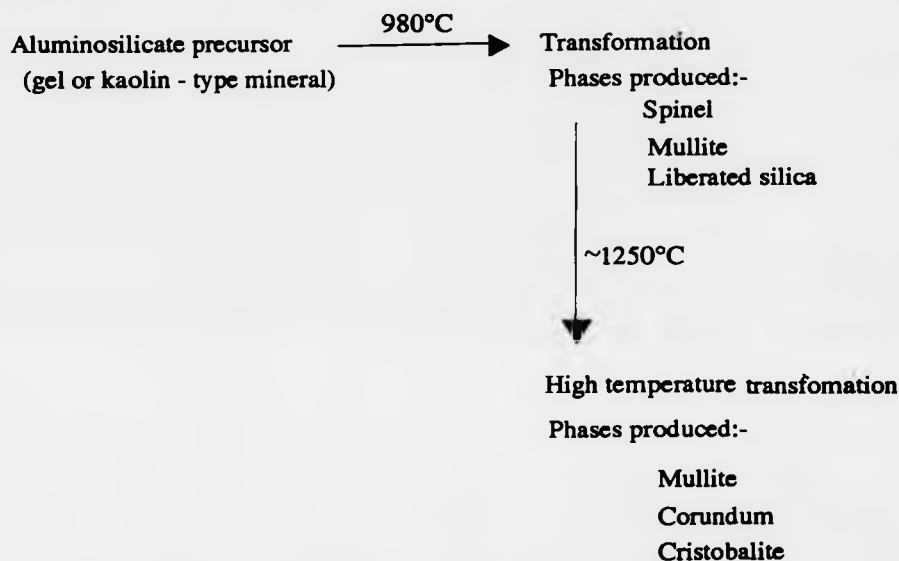


Figure 2.2. Summary of the crystallisation sequences of aluminosilicates

At about 1000°C the precursor material undergoes a transformation, the phases that are produced are a spinel, mullite and liberated silica. The level of homogeneity determines the amount of mullite and spinel produced, with more mullite being yielded with increasing homogeneity. The nature of the spinel phase has been widely debated, amorphous silica is thought to be liberated as a concurrent event with the formation of the spinel. The mullite is usually quoted as simply being mullite, with the implication that it is stoichiometric mullite, although this is questionable. At some higher temperature, usually between 1200°C - 1300°C a second transformation takes place. The nature of this event is very dependent on the lower temperature transformation, and hence the homogeneity of the precursor. Stoichiometric mullite is seen after this transformation, other phases that may be seen are corundum and occasionally cristobalite.

2.2.1 The 980°C transformation

These exothermic reactions can be followed using differential thermal analysis (DTA) equipment. The first exotherm is usually quoted as occurring at 980°C, although it has been quoted as occurring between 930°C and 1017°C. This event is observed when kaolin-type minerals [102,109-112], rapidly cooled glasses [99, 113] and sol - gel derived materials [21,68,78-84,88-97] are heated. The reason behind this exotherm has been widely debated in the literature and as yet no consensus has been reached. On completion of the exotherm, mullite as the sole crystalline phase has been observed [79,82,83,87,106,114]. Other workers have reported that the formation of a spinel phase is the reason for the exotherm [68,74,78-82,84,91,93,95,99,102,103,110,111,112,116,117, 118,129]. Other workers in the field have reported that the reason for this exotherm is the concurrent crystallisation of a spinel phase and mullite [80,82,86,89,94]. Colomban and Mazerolles [105] believe that the reason for the 980°C exotherm is an aluminium / silicon ordering reaction. This however gives no insight into the mechanism taking part and does not explain why different workers observe different behaviour. The nature of the spinel phase is itself a subject of debate, the situation is complicated in that the materials that have been used in the reported studies vary in composition, but more significantly they vary in structure prior to reaching the exotherm temperature. The differences in structure of the materials can be attributed to the method of synthesis, they range from inhomogeneous gels made by colloidal techniques [21,78,80,81,84,92-95,97] through the kaolin type minerals to the relatively homogeneous gels made via alkoxide sol - gel methods [68,78-84,88-91,93,96,97].

Okada and Ōtsuka [82] have developed a series of models to explain the crystallisation sequence in terms of the homogeneity of the material, the precursor structures are shown in Fig. 2.3. At the level of gross inhomogeneity, where alumina and silica powders are used, the particles crystallise independently with, eventually, a solid state reaction at the interface of the particles to give mullite. An increase in the level of homogeneity corresponds to coprecipitated gels. Regions that are silica or alumina rich exist on the atomic scale. On heating, these gels crystallise initially at 980°C in the alumina rich region to give a phase that is either a low temperature polymorph of alumina

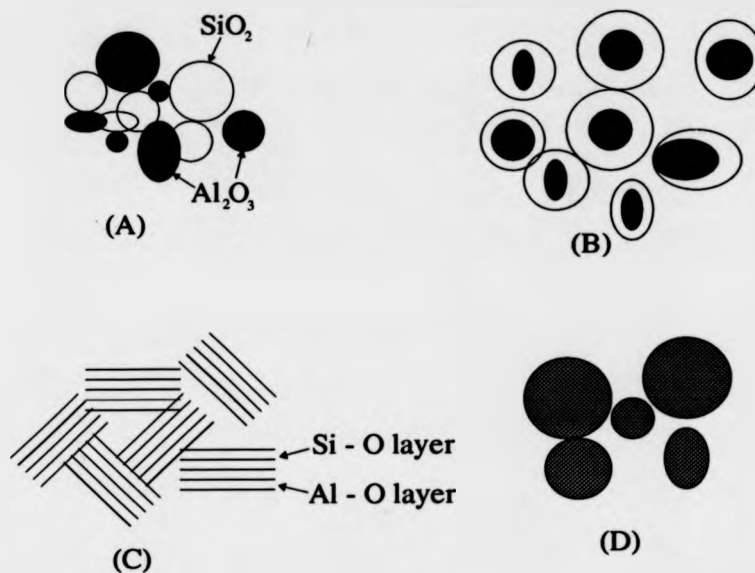


Figure 2.3. Schematic models of the structure of aluminosilicates, (A) silica and alumina particles, (B) coprecipitated gel, (C) kaolin type minerals and (D) mullite glass [after [82]].

(the γ form), or a spinel of composition $5.4\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. At the interface between the alumina and the silica rich regions some mullite may also be formed by a diffusion limiting reaction. Continued heating leads to the crystallisation of a stable silica phase, usually cristobalite. Heating still further gives a solid state reaction at the interface, again yielding mullite. Kaolin minerals have a crystallisation sequence similar to that of the coprecipitated gels. Due to their layered structure, random and intimate mixing between the coordination polyhedra of alumina and silica occurs in a direction normal to the planes of the layers. Within the planes of the layers however, there is zero mixing between the polyhedra of the two oxides. The final situation that Okada and Ôtsuka describe is that of totally random and intimate mixing of the oxides' polyhedra throughout the material. This is mullite glass. On heating to 980°C the direct crystallisation of mullite takes place. These models give a consistent explanation for the crystallisation behaviour of the materials involved but fail to provide a convincing mechanism.

Huling and Messing [115] believe that the reason behind the exotherm is the nucleation of spinel on $\gamma\text{-Al}_2\text{O}_3$. Slow hydrolysis allows the simultaneous incorporation of

alumina and silica into the network, this minimises the formation of the alumina rich regions which give rise to the spinel phase. Thus mullite is the crystalline phase that is produced on completion of the exotherm.

Okada and Ōtsuka prepared gels by rapid and slow hydrolysis routes, with, as would be expected from sol - gel considerations, the slow method yielding a more homogeneous gel. They also prepared gels of varying composition and recorded a variation in the exotherm magnitude with the Al/Si ratio. The homogeneous gels yielded the largest exotherm at $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, Hoffman *et al* [78] also report a similar increase in the magnitude of the exotherm with an increasing Al/Si ratio. Less homogeneous gels yield smaller exotherms [80,82,102] and sometimes no exotherm at all [78,81,116], although a continuous crystallisation over a temperature range of several hundred degrees has been reported [78].

2.2.2 Nature of the Spinel Phase

As briefly mentioned earlier yet another contentious issue arises from the 980°C exotherm, that is the composition of the spinel phase that is often, but not always, seen. The spread of opinion on this topic is typically very wide, with compositions ranging from $\gamma\text{-Al}_2\text{O}_3$ to $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ having been proposed. The issue can be simplified somewhat by asking whether the cubic spinel phase is $\gamma\text{-Al}_2\text{O}_3$ or whether it is an Al-Si spinel, that is a partially substituted cubic alumina. The bulk of opinion agrees that an Al-Si spinel is more likely, and this agrees with the various crystallisation models that have been proposed. However various works claim that cubic alumina is the phase responsible for the very broad and diffuse X-ray diffraction peaks at -45° and -67° (2 θ) [112,117,118]. Crofts and Marshall [91] point out that heating of an alumina sol derived from AlCl_3 to 800°C yields $\gamma\text{-Al}_2\text{O}_3$ this does not transform to $\alpha\text{-Al}_2\text{O}_3$ until heated to 1200°C for 2 hours. Hsi *et al* [81] point out that the homogeneity of the system also plays an important role, single phase gels they believe crystallise out to Al-Si spinel at the exotherm temperature. Less homogeneous gels transform via η - and θ - alumina at 300°C and 1200°C respectively, this kind of behaviour was also observed by Huling and Messing [80]. Most researchers believe however, that silicon atoms are substituted into the alumina

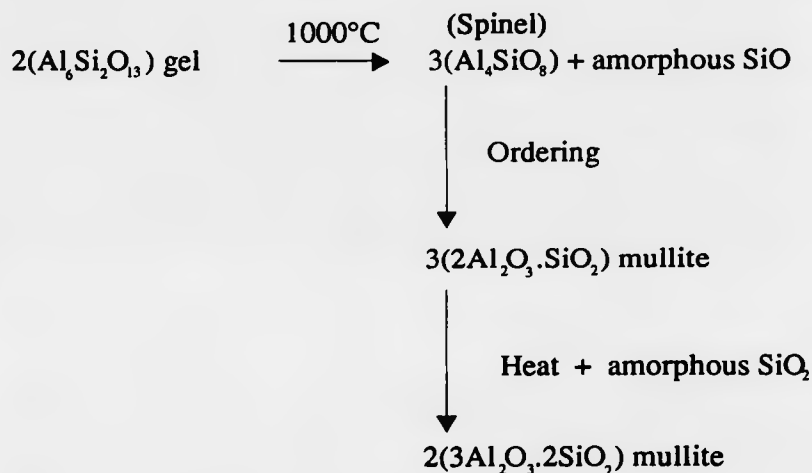
matrix to yield the spinel [74,76,82,110]. Okada and Ōtsuka [82] and Okada *et al* [110] point out that $\gamma\text{-Al}_2\text{O}_3$ transforms to $\alpha\text{-Al}_2\text{O}_3$ at 900 - 950°C, the presence of the cubic spinel phase to >1200°C indicates they believe that silicon is incorporated into the alumina stabilising it and they suggest a composition of approximately $6\text{Al}_2\text{O}_3\cdot\text{SiO}_2$. This composition, with about 8 wt% SiO_2 is in agreement with that estimated by Huling and Messing [115]. Leaching of kaolinite minerals and subsequent chemical analysis also suggests Al-Si spinel [110,119]. Chakraborty and Ghosh [119] suggest the spinel has the same composition as mullite [$3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$]. Okada *et al* [110] in a similar series of leaching experiments, suggest the spinel contains only 8 wt% SiO_2 , but say that if all the amorphous material is not removed prior to reheating a composition similar to that of Chakraborty and Ghosh is obtained. The technique used by Chakraborty and Ghosh has also been criticised on the grounds that it is not an accurate method for estimating the amount of free silica liberated during the kaolinite to mullite transformation [132].

Whatever the composition of the spinel phase, be it cubic alumina itself or a partially silica substituted polymorph of this alumina, it would appear that the phase is alumina rich.

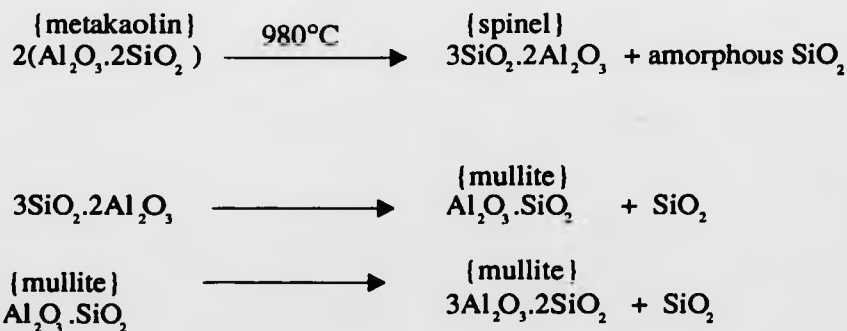
2.2.3 Mullite Formation

It is known that alumina rich ($2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) mullite forms from the melt and stoichiometric mullite forms in sintering reactions [101,104]. Chakraborty and Ghosh [119] reported that in the heating of kaolinite minerals to above the exotherm temperature mullite was formed. They also report that several lines from the diffraction pattern were missing, and the (120) and (210) reflections in particular were merged. Schneider and Ryman-Lipinsky [106] also report the formation of a mullite that also has these peaks merged. The material they made was derived from a sol - gel route with atmospheric moisture apparently being the source of water for hydrolysis. They report that this mullite is pseudotetragonal in contrast to the usual orthorhombic structure. Li and Thomson have [120] also found an alumina rich mullite after the 980°C exotherm. Cameron [104] determined that a relationship between the a_0 lattice parameter and the composition of mullite exists. As the amount of alumina in the mullite increases the a_0 lattice parameter increases. The point at which $a_0 = b_0$ has been estimated at 79 mol% Al_2O_3 . This

relationship between the composition and the lattice parameter is debated by Aramaki and Roy [103] who say that specific heat treatments have as much effect on the lattice parameters as does the composition. The linearity of Cameron's relationship has in general persuaded workers in the field of its validity. Low and McPherson [68], by sol - gel methods, have also formed the pseudotetragonal mullite on heating to 1000°C, they say that this mullite is alumina rich and based on Cameron's relationship is close to the composition $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. They derived the following reaction sequence to explain their findings.



This is similar, in that an alumina rich mullite is formed prior to the stoichiometric compound, to the reaction sequence described by Brindley and Nakahira [122,123,124], on the heating of metakaolin.



The conversion of the alumina rich mullite to stoichiometric mullite is the high temperature exothermic reaction referred to earlier. The alumina rich mullite reacts with the silica rich surroundings to yield stoichiometric mullite. This high temperature exotherm is also associated with the reaction of other alumina rich species with amorphous silica to yield stoichiometric mullite [80,81,84,94,117]. Huling and Messing [115] conclude that this exotherm is due to the release of alumina from its spinel type structure. They agree with Wei and Halloran [124] that the 3-dimensional growth is controlled by either short range diffusion or the reaction at the interface. Li and Thomson believe that the temperature of this exotherm follows an Avrami type model for inhomogeneous xerogels. This they believe may contradict Wei and Halloran in that longer range diffusion may need to take place in this model. This exotherm is more pronounced for less homogeneous systems where the reaction is between an alumina, often the spinel phase, and the amorphous silica rich phase. In the case of more homogeneous systems the reaction is between the alumina rich mullite and the amorphous silica to yield 3/2 mullite.

2.3 Structural Considerations

Amorphous aluminosilicates can provide three possible environments for aluminium. These are tetra-, penta-, and octahedral sites. the relative proportion of sites depends on the composition and more importantly, on the method of fabrication.

Materials produced by sol - gel techniques that are rich in alumina have octahedral aluminium as the favoured species [114,116,118,125]. As the amount of alumina falls the favoured coordination changes to tetrahedral [118,125]. The presence of Al(4) has been seen as evidence of condensation reactions [114,126], whilst Al(6) is seen as the result of a 3-D mechanism changing Al(4) to Al(6) [114].

The method of fabrication obviously affects the proportion of the environments for aluminium. When aluminosilicates are made using colloidal sol - gel methods Al(6) is the predominant coordination [116], as it is when a diphasic gel is made [125]. When the fabrication route involves the use of metal alkoxides or metal salts Al(4) sites are also present [114,116,126], and sometimes Al(5) is also observed. Sol - gel systems are not the only ones in which pentacoordinated aluminium is found, melt quenched aluminosilicate

glasses have also shown this polyhedron [87,113], a carefully dehydroxylated kaolinite sample has also shown Al(5) [111]. Selvaraj and co-workers suggest a distorted trigonal bipyramid structure for this polyhedron [126].

There exists a relationship between temperature (and also time at temperature), and the environments present. If we consider the case of Al(6) being essentially the sole environment [111,116,126], heating of the gel will promote Al(4) and even Al(5) coordination [111,126]. The material looked at by Sanz *et al* [111] was a silica rich kaolinite, this illustrates that this behaviour is common to aluminosilicates and is not simply a factor seen in sol - gel prepared samples. Yasumori *et al* [87] describe a sol - gel procedure where tetrahedral aluminium is the predominant coordination. On heating, the amount of octahedral aluminium increases until at 950°C pentahedral aluminium is observed. This behaviour seems to differ significantly from the previously described situation, with Al(6) growing at the expense of Al(4). The precursor used by Yasumori was an aluminium-silicon ester similar to that used by Pouxviel [114]. Pouxviel shows that the aluminium is tetracoordinated in the ester. Yasumori *et al* state that the xerogel is almost solely tetrahedral, but they do not give the temperature at which the xerogel was produced. The first temperature to which they refer for this gel is 400°C. At this temperature a significant amount of Al(6) could be seen, similar to the polymeric development in 3-D that Pouxviel *et al* propose for their ester based system. In general, in the systems that are relatively homogeneous, it can be said that on heating the proportion of pentacoordinate aluminium is increased. This behaviour continues on heating to 980°C, at this temperature the well known exotherm occurs.

As already mentioned, upon heating past the exotherm a crystallisation takes place, with either a cubic spinel type phase, mullite or both mullite and spinel being yielded. All reports of Al(5) suggest that this coordination state does not survive past the exotherm temperature. Where the predominant coordination prior to crystallisation at 980°C is octahedral, the major crystalline phase that is produced is the spinel [114,116,118]. Where significant amounts of tetrahedral and pentacoordinated aluminium are present, the major crystalline phase post 980°C is mullite. This was seen in the sol - gel systems [87,114] and in a quenched glass system [80]. When dealing with kaolinite minerals the coordination of

aluminium plays a secondary role to the effects of the layer structure in the role of crystallisation. Hence the material studied by Sanz *et al* [111] showed a significant amount of pentacoordinated aluminium, the the major crystalline phase after heating to above the exotherm temperature was spinel. Some workers have speculated on what happens to the pentacoordinated aluminium when this temperature is reached. Yasumori [87] concludes, that at the exotherm temperature, the Al(5) transforms to Al(4) and Al(6) due to a metastable phase separation. Sanz [111] agrees that the pentacoordinate aluminium is metastable, but believes that it transforms directly to Al(6). Selvaraj *et al* [126] conclude from their studies that the pentacoordinate state is a transition state between the octa- and tetrahedral states. The work done by Sanz *et al* also shows that a long time at a low temperature (36 hrs at 880°C) causes the disappearance of Al(5) and thus the 980°C exotherm is not seen with this material.

2.4 Post 980°C Structure

On completion of the exotherm there are two distinct aluminium coordination sites tetra- and octahedral. This situation is complicated by there apparently being two forms of tetrahedrally coordinated aluminium. There is one with an ^{27}Al MAS NMR resonance at approximately 60 ppm, the second is observed at about 42 ppm. Aluminium tetrahedra can give rise to resonances with chemical shifts between approximately 80 ppm for $\text{Al}(\text{OH})_4$ and 51 ppm for $\text{Q}^4(4\text{Si})$ in zeolites. Increasing the shielding about an aluminium atom causes a high field shift (that is to more negative chemical shifts). Increasing the number of bridging oxygens about the aluminium and substituting Si for Al as the nearest neighbour in the surrounding tetrahedra both cause a high field shift of an aluminium resonance [127]. Various workers have suggested reasons for the two tetrahedral resonances, these include the 60 ppm resonance being due to tetrahedral aluminium associated with vacancies, the 42 ppm resonance then being due to aluminium in non-oxygen deficient sites [111]. Yasumori *et al* [87] suggest that the following two types of tetrahedral environments may be responsible for the two resonances. Tetrahedra are available in mullite which can either be occupied solely by aluminium, Al^* , or by either aluminium or silicon atoms, T. These have mean interatomic Al - O distances of 1.77 - 1.85 Å and 1.66 -

1.73Å respectively. They suggest that the former gives the resonance at 60 ppm, the latter gives the one at 42 ppm. Turner *et al* [128] suggest that the 42 ppm resonance may be due to triclustered aluminium tetrahedra, similar to those proposed by Lacy [106], with oxygen being three coordinated by Al(4) and hence providing extra shielding of the aluminium.

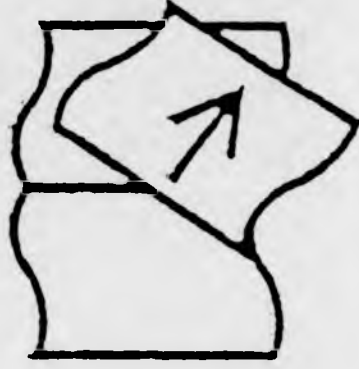
On completion of the 980°C exotherm the mullite produced has only a single XRD peak at approximately 3.42Å. This mullite has been called pseudotetragonal by Schneider and Rymon-Lipinsky [68], Low and McPherson [104] suggest that this pseudotetragonal mullite is alumina rich. On further heating a high temperature exotherm is observed, they say that this is due to the reaction of the alumina rich mullite with the silica rich matrix to yield stoichiometric mullite.

2.5 Densification

Table 2.1 gives the measured properties of some mullite samples, some of these being consolidated from sol - gel derived powders. These samples were all prepared by densifying at high temperature, and some under pressure as well. Relatively little data has been published on the low temperature sintering characteristics of mullite stoichiometry xerogels. Yoldas & Partlow [77] describe the results of the low temperature densification tests they carried out, when under pressure, or not, an homogeneous xerogel gives a massive shrinkage (35% linear shrinkage) at approximately 1000°C. For this material there was very little shrinkage below this temperature, this is in contrast to the inhomogeneous xerogel which shows a constant and gradual shrinkage with increasing temperature. Above 1000°C the shrinkage rate increases, the authors conclude that this is due to the action of free silica flowing viscously, they unfortunately neglect to record the final density they achieved. Rahaman *et al* [129] using supercritical drying methods created an aerogel and investigated the densification behaviour of this material. The sol - gel techniques they used led to a very inhomogeneous aerogel, this showed the same kind of viscous flow behaviour as the inhomogeneous gel of Yoldas & Partlow. They note that all densification had occurred below 1250°C, with the maximum rate occurring between 1100 - 1200°C. They then compacted an aerogel and heated it to 1200°C, holding at 1150°C and 1185°C, they held at all three temperatures for 1 hour. Using this method they achieved a sample with a density of 99% of the theoretical.

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Chapter 3

Experimental methods and techniques

3.1 Introduction

The central aim of this study was to develop a synthesis method for the production of mullite. In order to achieve this general aim the requirements of the material and the processing parameters must be stated;

- 1) The material must be synthesised at low temperatures.
- 2) Densification must be carried out at relatively low temperatures.
- 3) The densification process must yield a material that approaches the theoretical density.
- 4) On further heat treatment the material must crystallise to give mullite as the sole, or least the major, crystalline phase.

In order to satisfy these general requirements the technique of sol-gel was chosen as the most promising fabrication route. This particular route was chosen because of its use in producing glassy, or highly disordered materials at relatively low temperatures in comparison with traditional fabrication routes. Once the residual organics have been removed from the inorganic network built up by the sol-gel process, the advantages of having a glass for densification purposes can then be utilised. Glasses exhibit viscoelastic properties, especially at temperatures in excess of the glass transition temperature, that is they flow under applied pressure. This property can be used to enhance the density of a given glassy article to a value close or equal to, the theoretical. Thus if a fully dense glass of mullite stoichiometry could be achieved, the basic fabrication method and the optimum experimental parameters would be established. The incorporation of reinforcement agents at the powder or gel stage could then be carried out, the best case scenario would be that only minor modifications in the densification process would be needed. The material could then be heat treated to crystallise as mullite. That the matrix derived from the sol-gel method crystallises solely to mullite is important. Should the glass of mullite stoichiometry disproportionate into, for example, mullite, cristobalite and corundum the usefulness of the

article at high temperatures would be severely restricted. Mullite itself has a thermal coefficient of expansion, TCE, of $-5.6 \times 10^{-6} \text{ K}^{-1}$, cristobalite and corundum have TCE values of $27.0 \times 10^{-6} \text{ K}^{-1}$ and $8.8 \times 10^{-6} \text{ K}^{-1}$ respectively. Thus significant stresses would be set up if the article was thermally cycled. Cristobalite also undergoes a displacive transformation between its high and low forms at 220°C with an accompanying large volume change. Hence the production of a material that crystallises to a single phase, i.e. mullite is desirable, if not essential.

3.1.1 Synthesis

The development of any particular synthesis technique must start somewhere. Usually this is the replication, with or without minor modifications, of a previously reported method. The material is then characterised with the specific requirements of the ideal in mind. The likelihood is that the method needs to be changed to a greater or lesser extent to yield a material that comes closer to satisfying the requirements set down. Thus the synthesis method develops as the materials produced are characterised and classed as satisfactory or not. Small modifications in the procedure, such as the particular starting materials or the order in which they are introduced to the reaction vessel, need to be assessed. The incorporation into the general method of these modifications is determined by whether they yield a material closer to that desired than did the previous method. This leads to a spiral type of behaviour as the method is fine tuned to give the desired product.

The fabrication of mullite by sol-gel techniques has received a lot of attention in recent years, see chapters 1 & 2. There have been various approaches from a synthesis point of view and the major problem that has been encountered is the amount of mullite that is yielded at low temperatures. Most researchers obtained very high yields of mullite but only after heating the material to temperatures in excess of 1250°C . The material that they heated was also in the form of a powder.

The approach that was used in this study was to initially develop a material synthesis route that would crystallise solely to mullite. The problem of densification would then be tackled.

The experimental method that was used as the starting point was that developed by

Mizuno and Saito [16]. After observing the ability to produce mullite of a range of gels based on fumed silica and various aluminum sources, they concluded that the aluminium sulphate route was the most favourable.

3.2 Materials Processing

The major parameters that needed to be considered in the development of the material were the controllable, consistent and predictable crystallisation to mullite. On heat treatment at low temperatures the material must also densify to a value approaching the theoretical. In order to achieve this, several fabrication methods were developed.

3.2.1 The method of Mizuno and Saito

Mizuno and Saito [16] studied the formation of mullite from gels using fumed silica and various aluminium precursors. They semi-quantitatively estimated the relative amounts of mullite yielded from each of their samples after heat treatments at 1350°C and 1650°C. They concluded that aluminium sulphate $\{Al_2(SO_4)_3 \cdot 14-18H_2O\}$ as the aluminium precursor yielded the highest quality mullite. After densifying and crystallising the material they measured various mechanical properties, these are presented in table 2.1.

The method followed for this study involved forming a solution from aluminium sulphate hydrate, water and fumed silica. This solution was stirred for 10 hours and then dried at 120°C for 16 hours giving a cracked alcogel.

3.2.2 The method of Mazdiasni and Brown

Mazdiasni and Brown [11] developed a sol - gel based technique that yielded a powder that could be densified to greater than 99% at 1500°C under a uniaxial load of 34MPa. Mullite was the only phase they detected after this heat treatment, the mechanical properties of this material are presented in table 2.1.

Aluminium *iso*-propoxide $\{Al(OPr^i)_3\}$, tetraethyl silicate $\{Si(OEt)_4\}$, propan-2-ol and water were refluxed together for at least 16 hrs in order to achieve an homogeneous solution. The solution could be left open to the atmosphere to gel, alternatively the refluxed solution could be added slowly to a strongly basic (>20 vol%) ammonia solution. The

ammonia ions cause the peptization of the sols from solution. The peptized sols were then collected in a filter paper and washed in propan-2-ol under reduced pressure. This procedure yielded the basic alcogel which could then be characterised.

3.2.3 Sol deposition method

This method was indirectly developed from the technique of Mazdiyasni and Brown, and forms the general method used to produce most of the gels used in this study. The method will be outlined here but for clarity more specific variations of the method will be related at the start of the relevant results section.

Butan-1-ol was dehydrated by storing over aluminosilicate molecular sieve, the amount of the sieve used was approximately 30 vol% to maximise the amount of water removed from the alcohol. Aluminium iso-propoxide was dissolved in the dried alcohol, then tetraethyl silicate was added, the concentrations of these two alkoxides in the alcohol were 0.25M and 0.083M respectively. The solutions were covered and /or the procedure was carried out under a nitrogen atmosphere. The solutions were then stirred magnetically using a polypropylene, or a poly(tetrafluoroethylene) coated follower.

The sols were deposited by decanting a portion of the solution into a container to a depth of approximately 1mm, the volatile species from the solution were removed either by a flow of hot air being blown across the surface of the solution, or by placing the container into a drying oven at 120°C. After the removal of the volatiles a powder was left, this was the alcogel which could then be used for characterisation.

3.2.4 Xerogel Preparation

The basic method of obtaining a xerogel was to heat treat the alcogel in an air atmosphere with a ramping rate of 10°C/min to 800°C and a holding time of 5 hours. In certain specific cases other schedules were used and these will be discussed where relevant. This isothermal treatment was designed using the data obtained from thermal gravimetry and was intended to remove all chemisorbed organic species, leaving the amorphous network intact. This is the accepted description of a xerogel.

3.2.5 Densification

The general hot pressing parameters which were used are;

- 1) Graphite die with 1¼ inch internal diameter.
- 2) Alumina insert to the graphite die with an internal diameter of 1 inch.
- 3) 900°C pressing temperature.
- 4) Molybdenum discs 1 inch in diameter.
- 5) Alumina plunger and base.

The xerogel was ground and then cold pressed, uniaxially, into a 1 inch diameter disc. This was then sandwiched between the molybdenum discs in order to prevent reaction with, or adherence to, the alumina plunger or base. No lubricant was used since boron nitride, a commonly used lubricant, was found to act as a nucleating agent for the cubic spinel phase.

3.3 Characterisation techniques

3.3.1 Thermal analysis

On heating, all materials show some change. The nature of the change exhibited naturally depends on the material and can be classified into a few specific types. There may be a weight loss due to the desorption of physisorbed or chemisorbed species, possibly during a decomposition. A gain in weight may occur due to the reaction of the material with the atmosphere, for example oxidation. Structural changes in the material may also occur, these include polymorphic transformations from one crystallographic form to another. Amorphous materials may undergo several structural transformations, generally the first one is the glass transition. At temperatures below this transition the material is rigid and elastic, but without the long range atomic periodicity of crystalline materials, structural fluctuations are said to be "frozen in". At the glass transition temperature the amount of free volume associated with the material increases significantly, allowing translational motion of the coordination polyhedra. Above this temperature the material is said to be a supercooled liquid. The supercooled liquid may also crystallise, this is another example of a structural transformation with the material going from a metastable to a stable state at a particular temperature, or over a range of temperatures. A change of state, such as

melting, is the most dramatic and obvious structural transformation.

The variations in the character of the material undergoing heating, or cooling, can be investigated by a variety of techniques. The change in weight can be followed using a sensitive balance, the name of this general method is thermogravimetric analysis (T.G.A). To follow structural transformations it is necessary to understand their nature.

3.3.2 Structural transformations

When a structural change in a material is carried out there is a change in the enthalpy of the sample. The general relationship between the change in the free energy, ΔG , the enthalpy, ΔH , the temperature, T , and the entropy, ΔS , of the system is given by

$$\Delta G = \Delta H - T\Delta S \quad (3.1)$$

At the equilibrium temperature or pressure there is no free energy change on passing from one polymorph to the other, so eqn. 3.1 becomes zero. A first order transformation occurs when there is a discontinuity in the first derivative of eqn. 3.1, for example with respect to temperature.

$$dG / dT = -S \quad (3.2)$$

Entropy changes are difficult to detect themselves but since there is no change in the free energy, i.e. $\Delta G = 0$, we can rearrange eqn. 3.1.

$$\Delta S = \Delta H / T \quad (3.3)$$

Enthalpy changes can be easily measured by careful measurement of the temperature of the sample, for example by DTA. Second order transitions are those which cause a discontinuity of the second derivative of eqn. 3.1, for example;

$$\delta^2 G / \delta T^2 = -\delta S / \delta T_P = -C_P / T \quad (3.4)$$

Second order transitions are more difficult to detect as they involve far smaller amounts of energy than first order transitions. The glass transition in amorphous materials is similar to this type of transformation. It is exhibited in Differential Thermal Analysis as a shift in the base line.

3.3.3 Thermal analysis - Experimental design

The crudest form of thermal analyser consists of a heating block in which the sample is placed, and a thermometer is placed in contact with the sample. On heating at the temperature of a thermal event, the sample will be at a different temperature than the heating block. Assuming a linear heating rate the event will be identified as a deviation from linearity, this is shown in fig. 3.1(a).

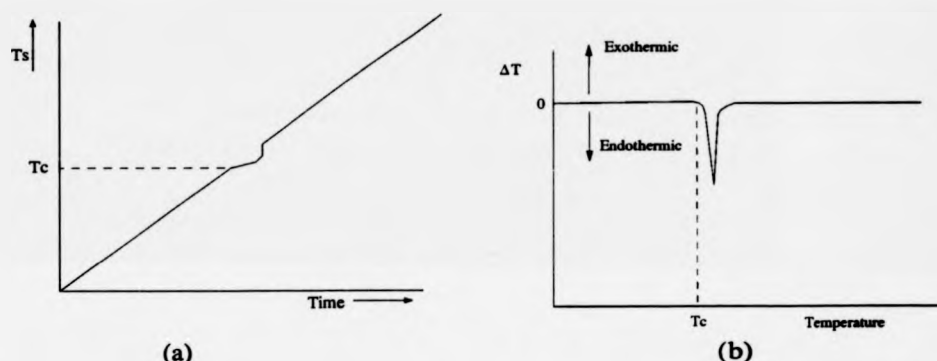


Fig. 3.1 Detection of thermal events, (a) direct measurement of the sample temperature, (b) comparison of the sample temperature with an inert reference.

A more sensitive method of detection of thermal events involves comparing the temperature of the sample with that of an inert reference material in the same heating chamber and so undergoing an identical heating (cooling) schedule. This technique increases the sensitivity of the system and allows any non-linearities that occur to be classified as thermal events due to the sample or external effects. The difference in temperature between the sample and the reference can be collected electronically and amplified. The kind of signal produced is shown in fig. 3.1(b).

There are two forms of differential thermal analyser, the most common kind is simply called a DTA, the more quantitative design is called the Differential Scanning Calorimeter (DSC). The two main differences between these pieces of equipment is in the design of the sample holder, and in the method of maintaining parity between sample and reference and the associated signal collection. The crucible that is used in the DTA equipment has a

dimple in its base, the thermocouple head goes into this dimple. A flatter crucible is used for DSC equipment, this is because the two crucibles are maintained at the same temperature by supplying heat to the cooler of the cells during a thermal event. It is the amount of energy that is supplied to regain parity between the two that is measured and this leads to the more quantitative nature of DSC over DTA.

3.3.4 Thermogravimetric Analysis - Experimental Conditions

The variation in weight of the samples on heating was carried out using a Stanton Redcroft Differential Thermogravimetric Analyser model TG - 750. This shown in fig. 3.2. This equipment was used in the balance mode, that is a plot of the weight of the sample against the temperature was obtained.

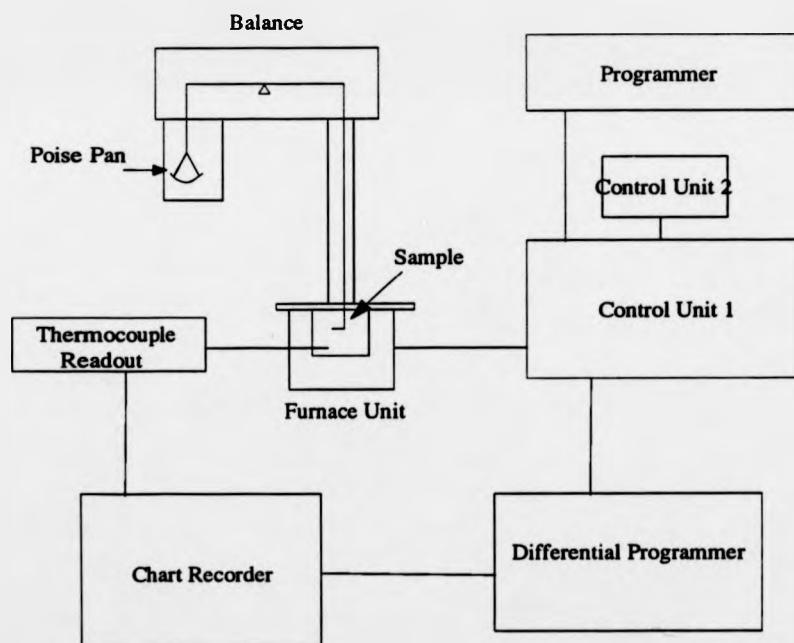


Fig. 3.2 Schematic representation of the thermogravimetric arrangement used.

This method of analysis was used primarily to determine the temperature at which all volatile materials had been removed from the sol - gel powders. The conditions under which these determinations were run were, for a general case, a heating rate of $10^{\circ}\text{C}/\text{min}$, a static air atmosphere, the crucible was made out of platinum.

3.3.5 Differential Thermal Analysis - Experimental Conditions

The initial thermal analysis was carried out using a Stanton Redcroft DTA model 673 - 4, with a high temperature head capable of reaching 1500°C. A linear temperature variable rate programmer was used and typically runs were carried out at 10°C/min in a static air atmosphere using either platinum-rhodium or alumina crucibles. The reference sample used was always quartz, usually Limoges quartz, the quartz also acted as an internal standard for temperature since at 573°C there is a well documented and characterised $\alpha \rightarrow \beta$ transition occurring. This transition is endothermic, with increasing temperature, but since the quartz is the reference it appears on the recording as an exotherm.

A second thermal analyser became available during the course of the study, this was a Netzche DSC type 404, with programmer type 410, this is shown in fig. 3.3.

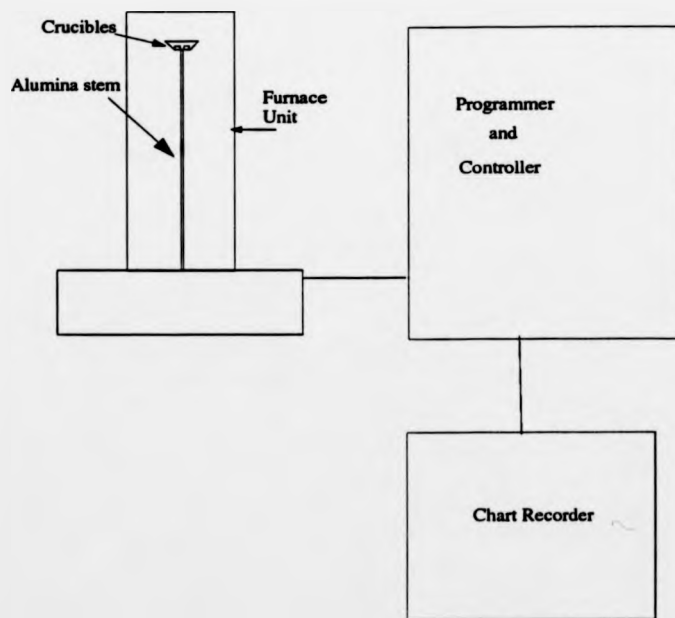


Fig. 3.3. Schematic diagram of the differential thermal analysis arrangement used.

This equipment was only run using the high temperature arrangement, capable of 1500°C. Alumina crucibles only were used, with a static air atmosphere, in order to

increase the rate of analyses done a varying heating rate schedule was used. This was typically;

20°C -> 850°C @ 25°C / min

850°C -> 900°C @ 5°C / min

900°C -> 1025°C @ 10°C / min

3.4 Structural Characterisation

3.4.1 X-ray diffraction (XRD)

To determine whether individual samples were amorphous or crystalline and which phases were present, they were analysed by x-ray diffraction. This well established technique involves irradiating the sample with well characterised radiation and where long range order exists on an atomic scale, the diffracted radiation undergoes interference. When the angle θ , between the incident x-rays of wavelength λ and a series of parallel planes of atoms with a separation d , between the planes satisfies Bragg's law;

$$n\lambda = 2d_{hkl}\sin\theta \quad (3.5)$$

the interference is constructive and intensity maxima are observed. The subscript hkl on the term for the plane spacing simply defines the direction of the plane in the notation of Miller indices.

There are various techniques used for the detection of the intensity maxima, the most widely used is the diffractometer method. The detector and the source of the x-rays define a circle known as the diffractometer circle, the specimen is placed at the centre of this circle at an angle of θ to the incident x-rays, the diffracted radiation is at an angle θ to this giving a total angle between the incident and diffracted photons of 2θ . The detector is usually a Geiger-Müller tube, this is rotated along an arc of the diffraction circle at a velocity of 2ω , the sample is rotated at an angular velocity of ω . Thus an angle of 2θ is always maintained between the incident and diffracted x-rays. The system used during this study is based on the same principle, the sample however was static. The detector was also static but instead of being effectively a point detector such as a Geiger-Müller tube, it covered an arc of the diffraction circle of 120° . Since powder samples were being used they can be thought of as containing crystallites in every orientation randomly arranged,

thus the characteristic diffraction pattern of the material is observed.

The instrumental set-up used is shown in fig. 3.4, the detector is an Inel Curved Position Sensitive CPS 120 system. The detector consists of a central wire, the anode, which has a potential difference of -9.6 kV placed across it relative to the cathode. The detector works on the same principle as a Geiger-Müller tube, with an interior gas that is

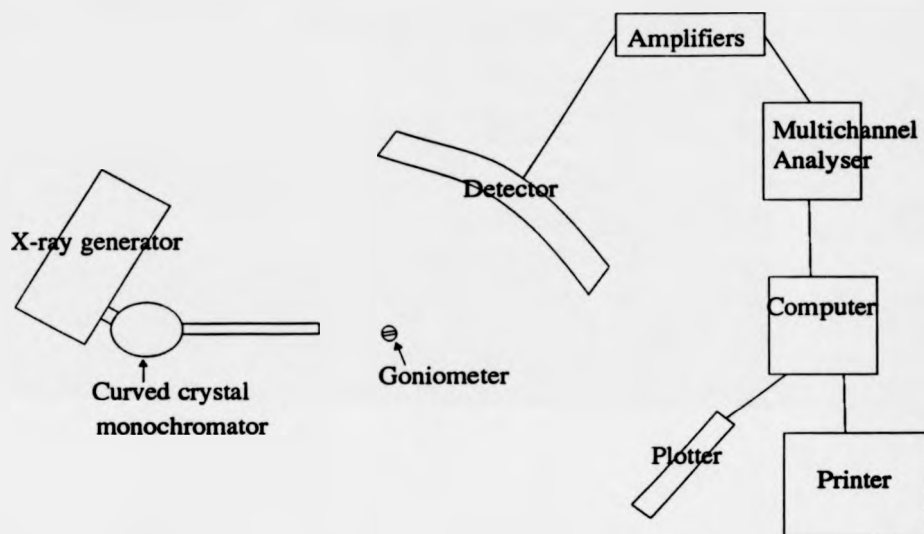


Fig. 3.4. Schematic diagram showing the arrangement of the XRD equipment used.

dissociated by x-rays, and the potential gradient causing an avalanche effect as the ions move towards the anode and cathode. The gas that is used is 15 vol% ethane in argon, this flows through the detector chamber at approximately 35 cm³ / min. The signal generated is amplified and collected by a Silena Varro multichannel analyser, this is then transferred to a Dell personal computer and analysed using Inel 'Diffractinel' software.

3.4.2 Magic Angle Spinning Nuclear Magnetic Resonance (MASNMR)

NMR is a technique that allows the local environment of particular nucleus to be probed. Certain nuclei when in a strong magnetic field will characteristically absorb energy when irradiated by a second, weaker, magnetic field. The absorption occurs when the nuclei become realigned within the magnetic field. The resonances that occur in liquids do

so over a short band width, that is the distribution of frequencies where resonance occurs is small. The spectra that are obtained from liquid samples are said to have narrow resonance lines. The resonances from solids are significantly broader, this is due to various static anisotropic interactions such as dipolar interactions, symmetry effects, quadrupolar interactions for nuclei with spin $I > \frac{1}{2}$ etc. The reason for the difference in the line width of resonances in solids and liquids is that the major structural broadening interactions have a $3 \cos^2\theta - 1$ angular dependence. Liquids, due to their inherent structural isotropy and the random Brownian motion which averages this angular dependence to zero, consequently have rather narrow resonance band widths. When solids are spun at a particular angle where $\cos\theta = 1/(3)^{1/2}$ ($54^\circ 44' 7''$), the so-called Magic Angle, a significant reduction in the line width can be achieved. This is because the structural anisotropies that cause some of the line broadening are averaged out and the angular dependence term equals zero. This reduction in the line width is important since a very broad line may mask some of the structural information contained within the signal. It is this technique of spinning the sample and obtaining better resolved spectra that has allowed the technique to be extended to solid samples, and thus has increased the scope of NMR and made it into a much more powerful and useful tool.

The resonance frequency of a nucleus is dependent on the detailed state of its local chemical environment. Factors that influence this environment include the coordination number of the target nuclei, bond length, angle and the nature of the first and second nearest neighbours in particular and the length and angle of the bonds to the nearest neighbour. The bonding characteristics mentioned are particularly relevant when glasses are being investigated. The lack of long range order of these materials gives rise to a broad resonance when compared to that obtained from the corresponding crystalline material.

The ^{27}Al MAS NMR spectra were taken on a Bruker MSL spectrometer operating at 8.45T. A homemade probe was used, with the samples being spun at approximately 7kHz using compressed air as the driving force. The spinners used were made out of silicon nitride with Vespel caps with an external diameter of 5mm. The spectra were obtained at 93.83 MHz with a $1.0\mu\text{s}$ pulse repeated every 1.0s. The chemical shifts were recorded with respect to an aqueous AlCl_3 solution.

3.5 Density measurements

3.5.1 Bulk samples

The densities of bulk samples prepared by sintering or hot pressing were determined by the Archimedes' principle. The sample, of known weight, was suspended from the pan support of the balance using very fine copper wire, it was then completely immersed in the displacement liquid, the weight being taken soon after immersion, distilled water was used throughout. The relationship used to calculate the density was

$$\rho_s = W_s (\text{in air}) \cdot \rho_l / \{ W_{w+s} (\text{in air}) - W_{w+s} (\text{in water}) \} \quad (3.6)$$

where ρ is the density and W is the measured weight, the subscripts s , l and w refer to the sample, the liquid and the wire respectively. Thus the overall bulk density does not include those pores that are large enough for the displacement liquid to readily fill.

3.5.2 Powder samples

The powder to be weighed was placed in a dry weighing bottle of known weight and volume and weighed, the bottle was then partially filled with distilled water. The bottle was allowed to stand for approximately 1 hour to allow all accessible porosity to be filled with water. The bottle was then agitated by hand and also by low power ultrasound for approximately 10 minutes to dislodge any air bubbles. After allowing the powder to settle to the bottom of the bottle, the bottle was carefully filled with distilled water. The lid (which has a hole in it) was then carefully placed on top of the bottle ensuring that no air bubbles were trapped. All moisture was removed from the outside of the bottle, and the bottle was immediately weighed so as to minimise errors due to the loss of water from the lid due to evaporation. The relationship used to calculate the density of the samples was

$$\rho_s = W_s \cdot \rho_l / \{ W_l - (W_{b+l+s} - W_{b+s}) \} \quad (3.7)$$

where ρ is the density, W is the measured weight, the subscripts s , l , and b refer to the sample powder, displacing liquid and bottle respectively. This method measures the skeletal density, the powder nature of the samples should allow the liquid access to most of the porosity that was closed in the bulk article.

Chapter 4

Results:

Materials synthesis and characterisation

4.1 The method of Mizuno and Saito [93]

The preparation techniques of Mizuno and Saito were followed, giving gels which could then be characterised by methods other than those reported [see section 3.2.1].

4.1.1 Results - Thermal analysis

The cracked gel that was produced by the fabrication lost weight on heating in two distinct stages. The thermogravimetric trace, fig. 4.1, shows that the low temperature weight loss is gradual and quite constant to approximately 390°C. The weight of the sample drops slightly on heating to 790°C and then a rapid weight loss is observed on further heating. The upper temperature limit of this change was not observed with the equipment available, differential thermal analysis however suggests a temperature of -960°C, fig 4.2. The low temperature weight loss is due to the loss of water and volatile organics, the high temperature loss is due to the decomposition of unreacted aluminium sulphate, 770°C is the decomposition temperature for the pure compound [133].

4.1.2 X-ray diffraction

The dried cracked gel had aluminium sulphate hydrate present in a crystalline form even after being heated at 600°C for 4 hours. The presence of any crystalline silicon containing phases was not detected either in the dried gel or after the 600°C treatment. Fully crystalline orthorhombic mullite was the only crystalline phase detected after the material had been heated for 16 hours at 1150°C, fig. 4.3.

4.1.3 Discussion

The Mizuno technique involved the use of aluminium sulphate hydrate which did not go fully into solution and this compound did not start to decompose below 790°C. This method does not facilitate the production of a fully homogeneous gel, and so was rejected

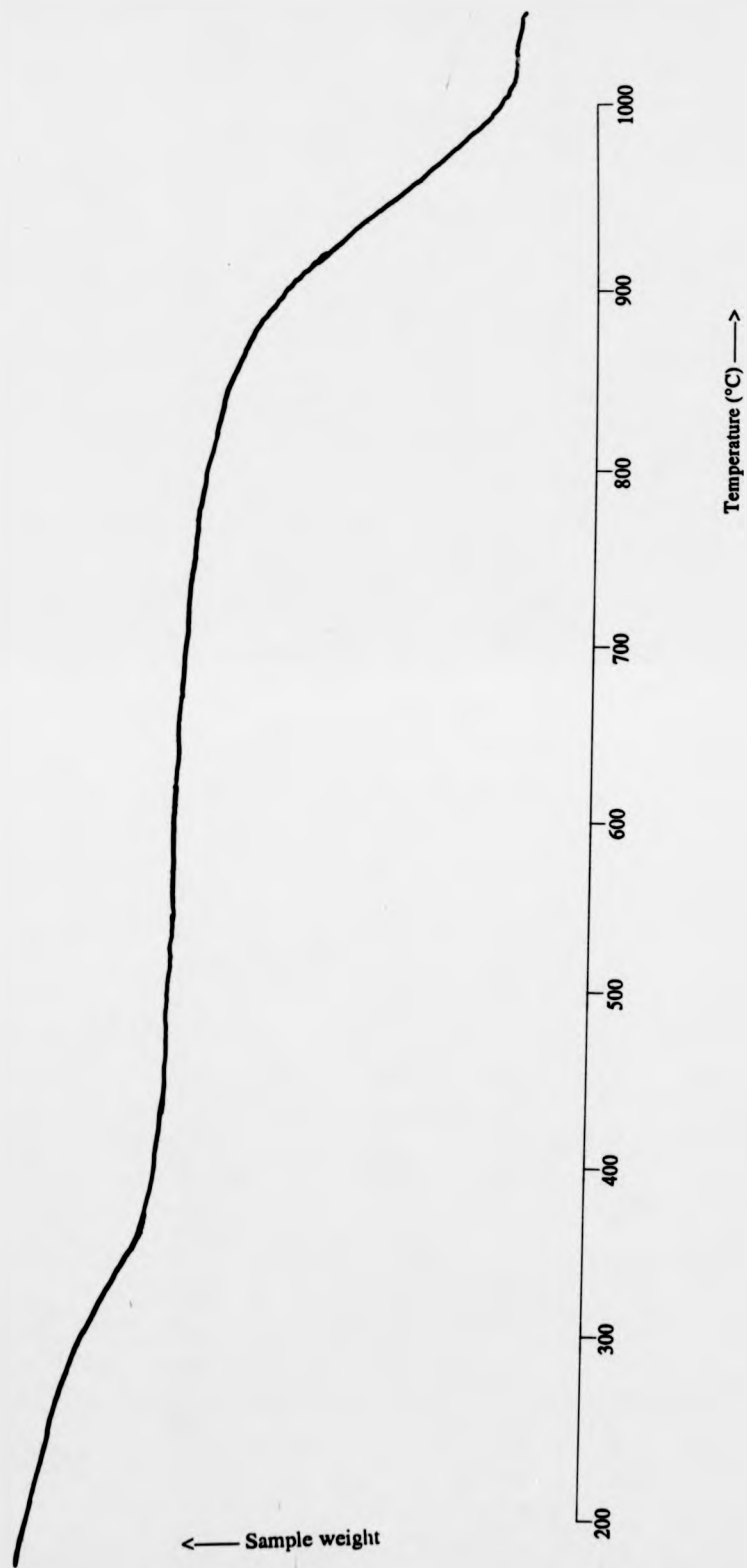


Figure 4.1) The thermogravimetric behaviour of an alcogel prepared using the method of Saito and Mizuno.

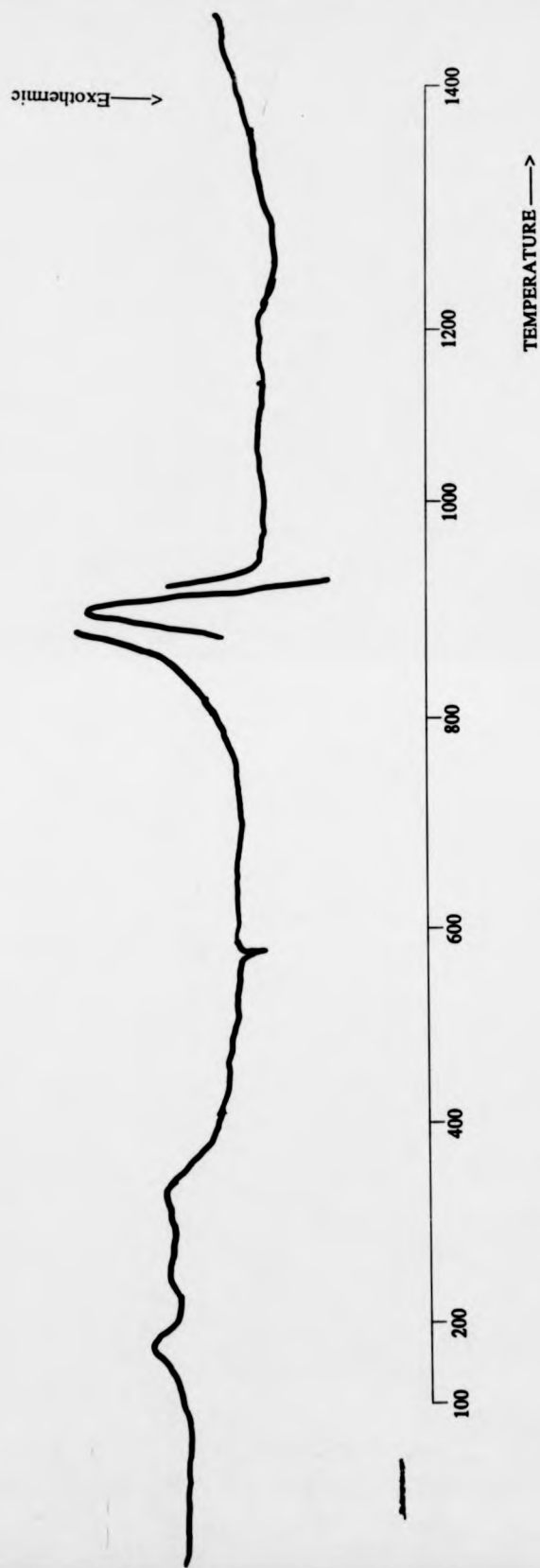


Figure 4.2) The differential thermal analysis behaviour of a xerogel prepared by the method of Mizuno and Saito.

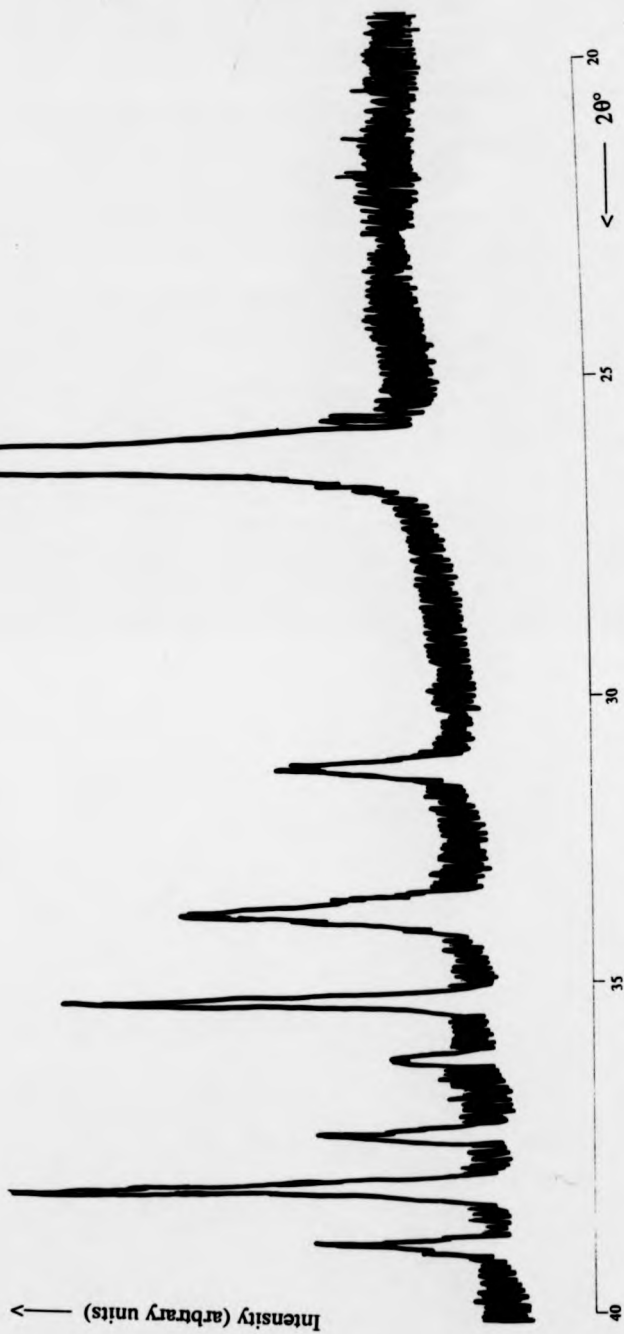


Figure 4.3) The X-ray diffraction pattern of material prepared by the method of Mizuno and Saito and then heat treated at 1150°C for 16 hours. All the peaks are due to orthorhombic mullite.

as a basis for producing an amorphous article of mullite stoichiometry that could be densified at low temperatures.

4.2 The method of Mazdiyasni and Brown [90]

Since the method of Mizuno and Saito did not appear to produce a material that was compatible with the aims of this project a different preparation technique was attempted. The method of Mazdiyasni and Brown is an alkoxide based route and as such does not present any decomposition problems. It also allows the polymeric sol-gel route to be followed.

As described in section 3.2.2, two methods of achieving an alcogel from the basic procedure were used. One was to cause the peptization of the sols the other was to allow the solution contact with atmospheric humidity.

4.2.1 Peptized material - Thermal Analysis

The peptized material shows a significant loss in weight on heating, the thermogravimetric trace of this material is shown in fig. 4.4. Fig. 4.5 shows the corresponding DTA trace of the material, over a larger temperature range. The effect of temperature on the weight of the sample falls into two distinct regions or stages. The first, low temperature stage, to -100°C is large and dramatic, this weight loss is an endothermic event indicating evaporation of physisorbed water. The water has two possible sources, it is evolved during the condensation reactions as the sols are generated and water from the peptizing solution may have been trapped as the sols coalesced and precipitated. The second stage is a gradual and slight weight loss above -100°C . This is accompanied by endothermic behaviour over the temperature range $250 - 320^{\circ}\text{C}$ indicating the loss of relatively free organic compounds by volatilisation and evaporation. continued heating of this material yields a very small exotherm at about 1100°C .

4.2.2. X-Ray Diffraction

Fig. 4.6 shows a section of the x-ray diffraction pattern of the peptized material after drying at 200°C for 2 hours. The sharp peaks are due to bayerite ($\text{Al}(\text{OH})_3$) the broad

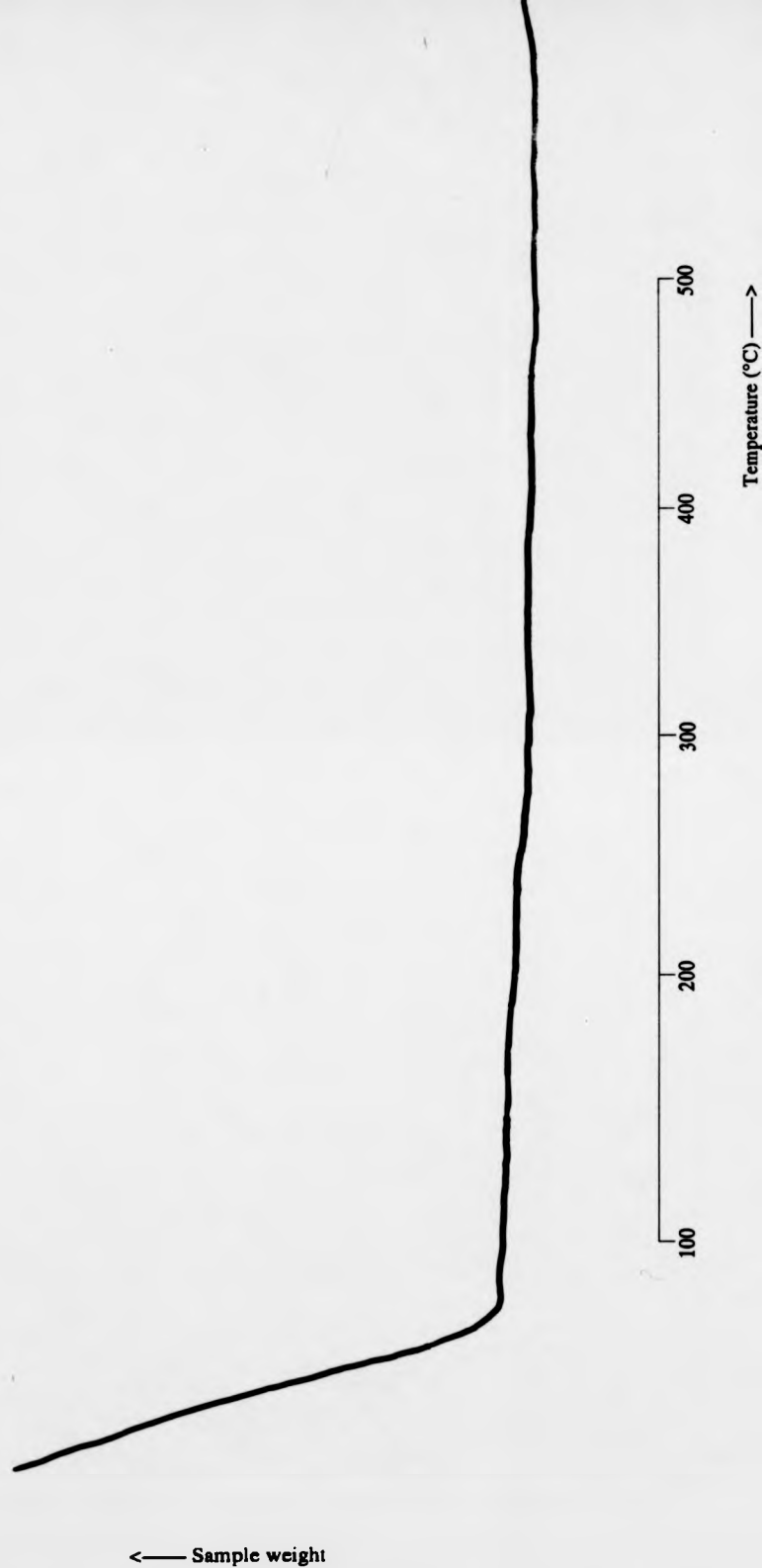


Figure 4.4) Thermogravimetric behaviour of an alcogel prepared by
peptizing the alkoxide / alcohol solution.

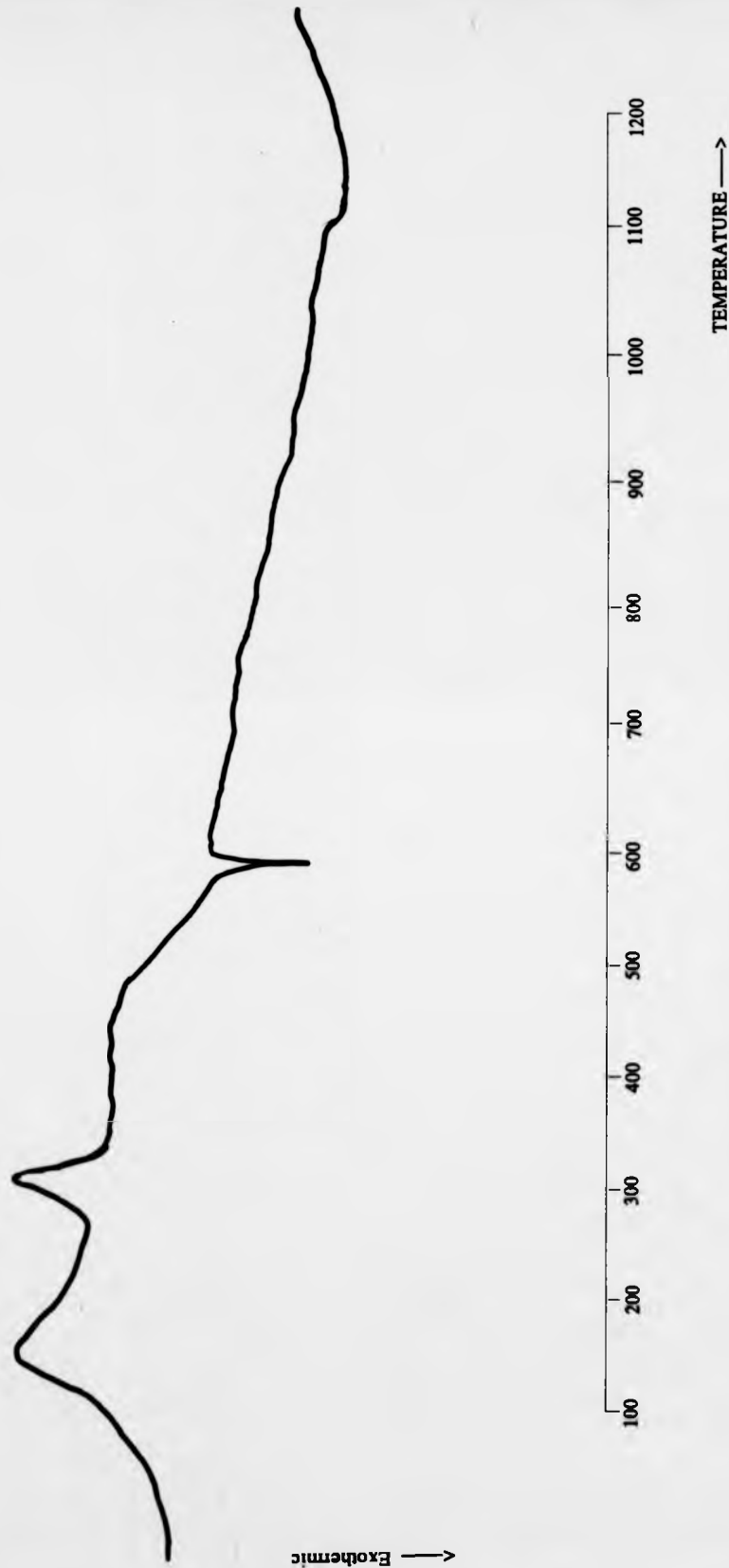


Figure 4.5) Differential thermal analysis trace of the alcogel made by
peptization of the alcohol / alkoxide solution.

Intensity (arbitrary units) ↑

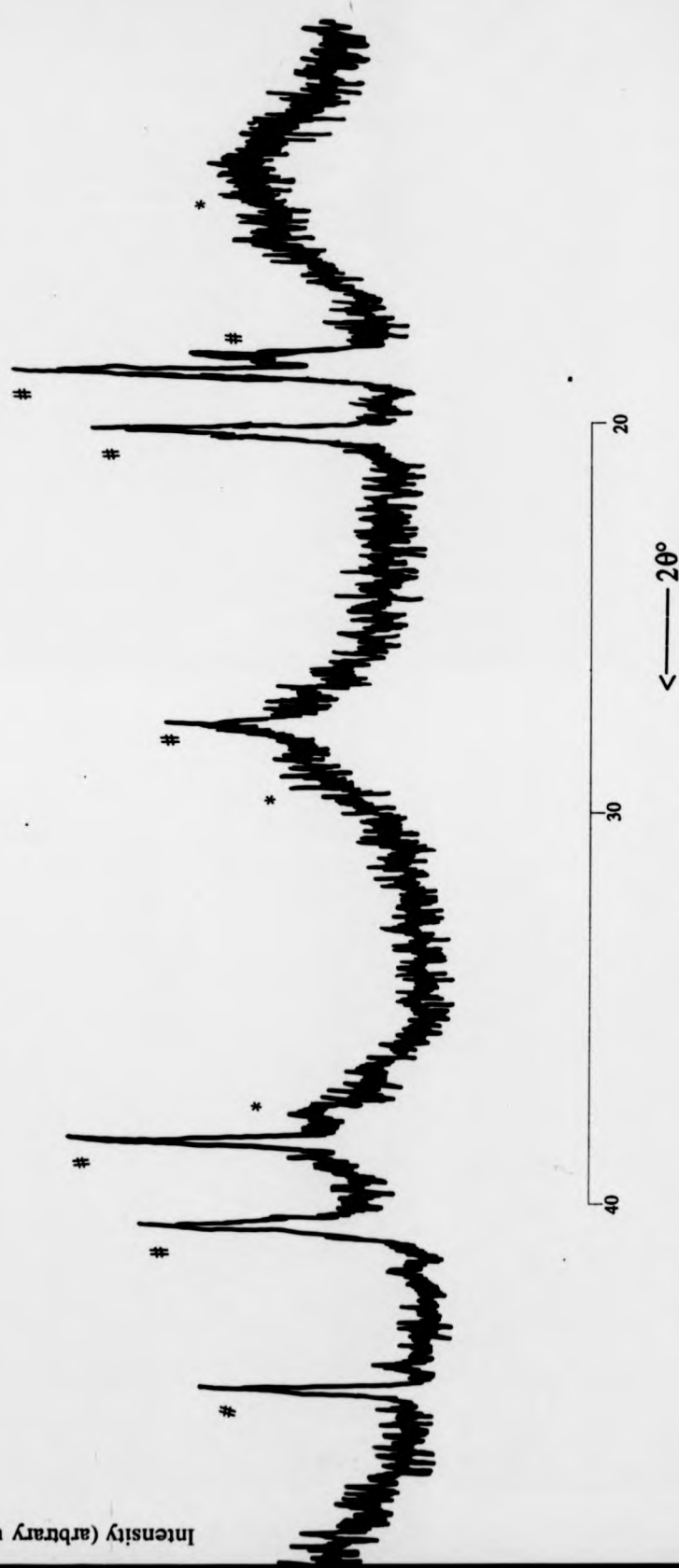


Figure 4.6) X-ray diffraction pattern of the pepitized material after heat treating at 200°C for 2 hours. The peaks labelled * are due to boehmite and the peaks labelled # are due to bayerite.

peaks are due to boehmite (γ -AlOOH) and the width of these peaks indicates very small crystallites. Assuming that the broadening of these peaks is caused solely by crystallite size considerations the average crystallite size may be calculated using the relationship;

$$t = 0.9\lambda / (B \cos \theta_B) \quad (4.1)$$

where t is the size of the crystal, λ is the wavelength of the x-rays, B is the angular width of the diffraction maximum at half peak height (in radians) and θ_B is the position of the maximum, in terms of 2θ . From the peak widths of the boehmite diffraction maxima it was estimated that the average crystallite size was approximately 50Å.

It should be noted that no silicon species are indicated as being present in the crystalline phases that were detected after this low temperature heat treatment. Further heating of the material, to 1400°C for 18 hours, yields a material that has the XRD pattern of fig.4.7. This spectrum shows the presence of two crystalline phases, corundum (α -Al₂O₃) and mullite.

4.2.3 Discussion

The low temperature heat treatment of this material gave rise to the crystalline hydroxy and oxyhydroxy polymorphs of alumina. Yoldas [75] found that these polymorphs were generated when an aluminium alkoxide (sec-butoxide) was hydrolysed in excess water. Thus this route has yielded an inhomogeneous material, the aluminium and silicon coordination polyhedra are segregated. Continued heating of this material yields mullite and corundum, this indicates the level of inhomogeneity of the material since the alumina and silica rich regions have not fully reacted together.

4.2.4 Gelled material

A solution was prepared following the method of Mazdiyasn and Brown [90]. Instead of peptizing this solution however it was left open to the atmosphere to gel.

4.2.5 Thermal analysis - results

After gelling, this material was allowed to age whilst open to the atmosphere. The material cracked and collapsed to a powder. As the liquid trapped within these pores

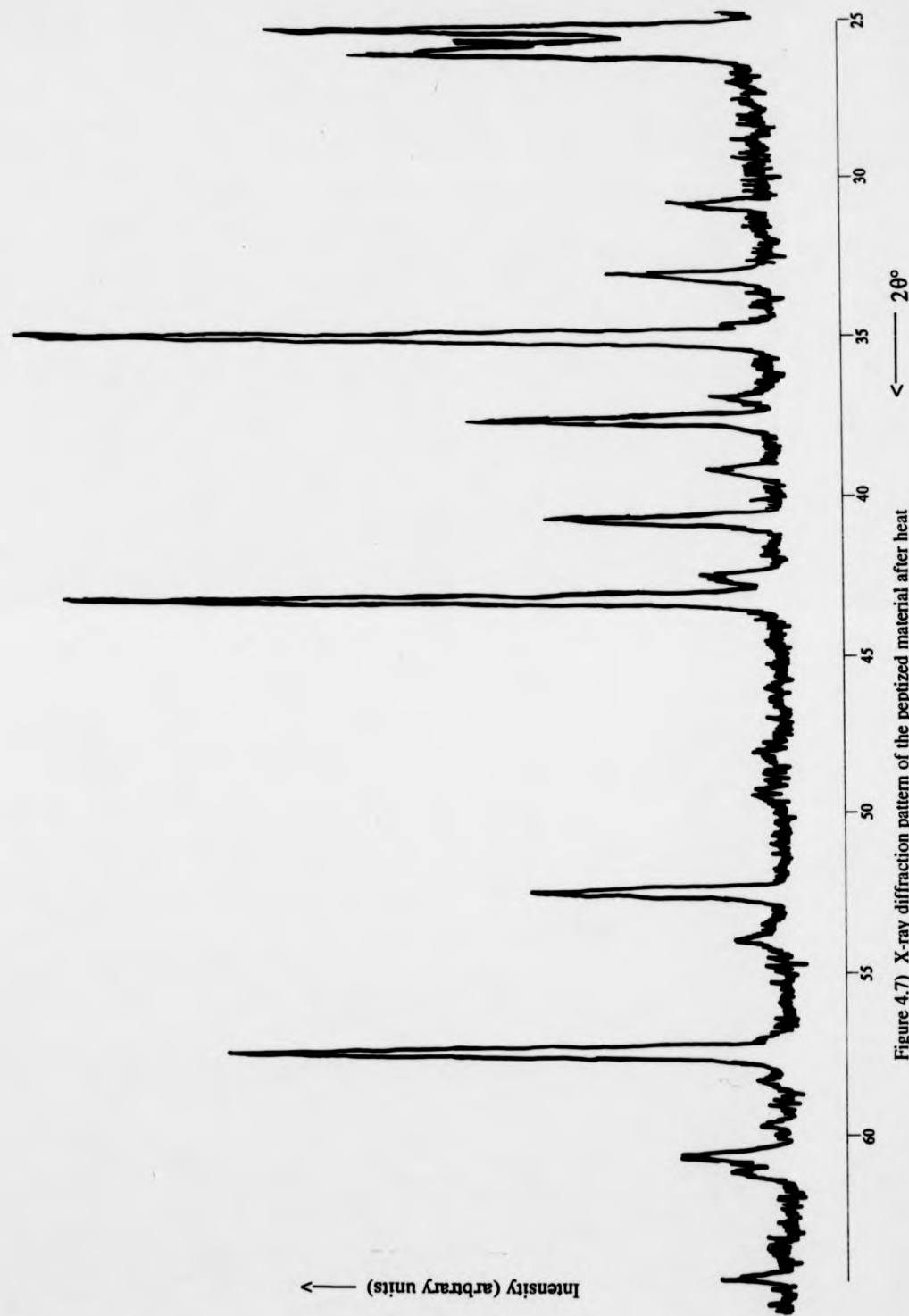


Figure 4.7) X-ray diffraction pattern of the peptized material after heat treating at 1400°C for 18 hours.

evaporates, differential stresses are set up due to the range of capillary forces resulting from the pore size distribution. It is these stresses that cause the material to crack.

Thermogravimetric analysis of this material showed that it behaves differently from the peptized material, fig. 4.8. A gradual but significant weight loss is seen to occur from room temperature to approximately 600°C. This indicates that the weight loss is not due to the loss of a specific compound but probably due to a range of compounds. These compounds will be physisorbed and chemisorbed organics from the alkoxides and the alcohol, they will also include species that have evolved during the condensation of the alkoxides. According to Schmidt [3], they will probably also include ethers that are liberated by condensation at moderate temperatures, 200 - 400°C.

The DTA trace of this material, fig. 4.9 shows a very sharp peak occurring at 986°C, x-ray diffraction of the sample after completion of this exotherm yields a single phase - mullite, fig. 4.10. Prior to any heat treatments the material contained no detectable crystalline phases.

4.2.6 Discussion

The difference in the two materials produced by peptizing the alkoxide/alcohol solution and allowing hydrolysis to occur using atmospheric humidity is quite marked. Introducing the solution into water causes the aluminium alkoxide to preferentially hydrolyse. The species produced by this hydrolysis then self-polymerise forming alumina rich regions, thus decreasing the overall homogeneity of the material. The slow hydrolysis method by contrast yields a material that is homogeneous in that it is amorphous to x-rays after low temperature heat treatments, and the phase that is yielded at the exotherm temperature is mullite. The value of limiting the amount of water available to the system, or at least the rate at which it is introduced to the system is therefore clear. The method that involved the peptization of the solution, giving rise to low temperature crystalline phases, was therefore rejected on the basis of the inhomogeneous nature of the material it produced.

The route involving the gelation of the solution was considered to be the most promising technique and was used as the basis for further material fabrication.

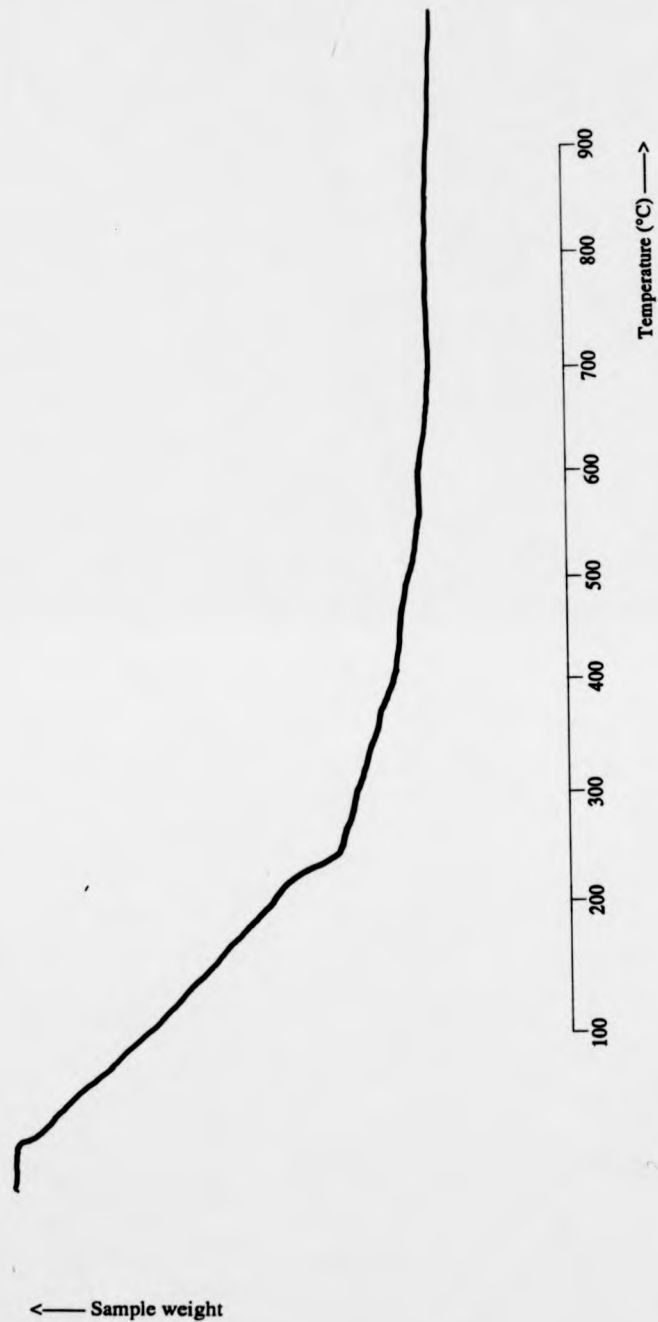


Figure 4.8) Thermogravimetric behaviour of the gelled alkoxide / alcohol solution.

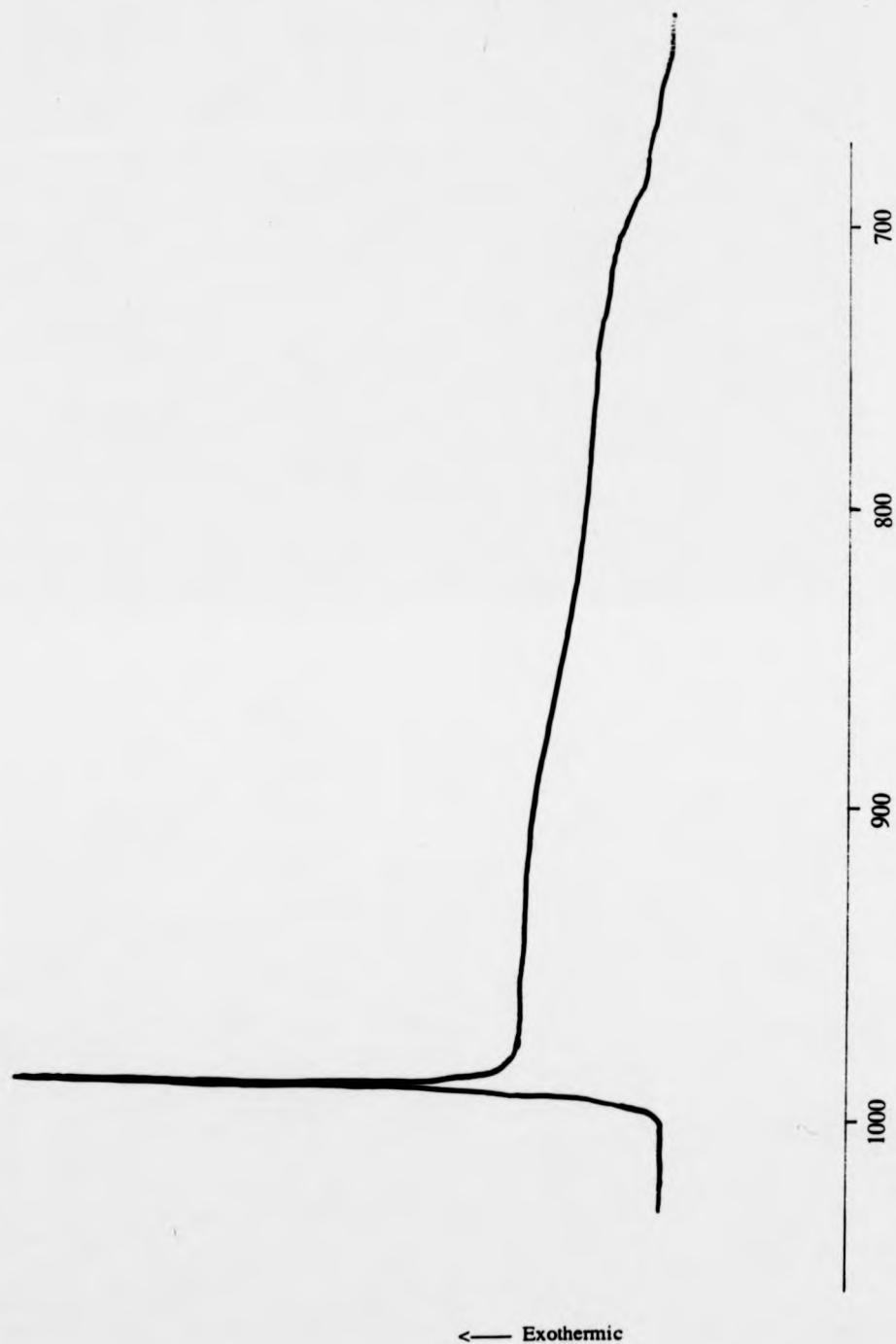


Figure 4.9) Differential thermal analysis behaviour of the gelled alkoxide / alcohol material.

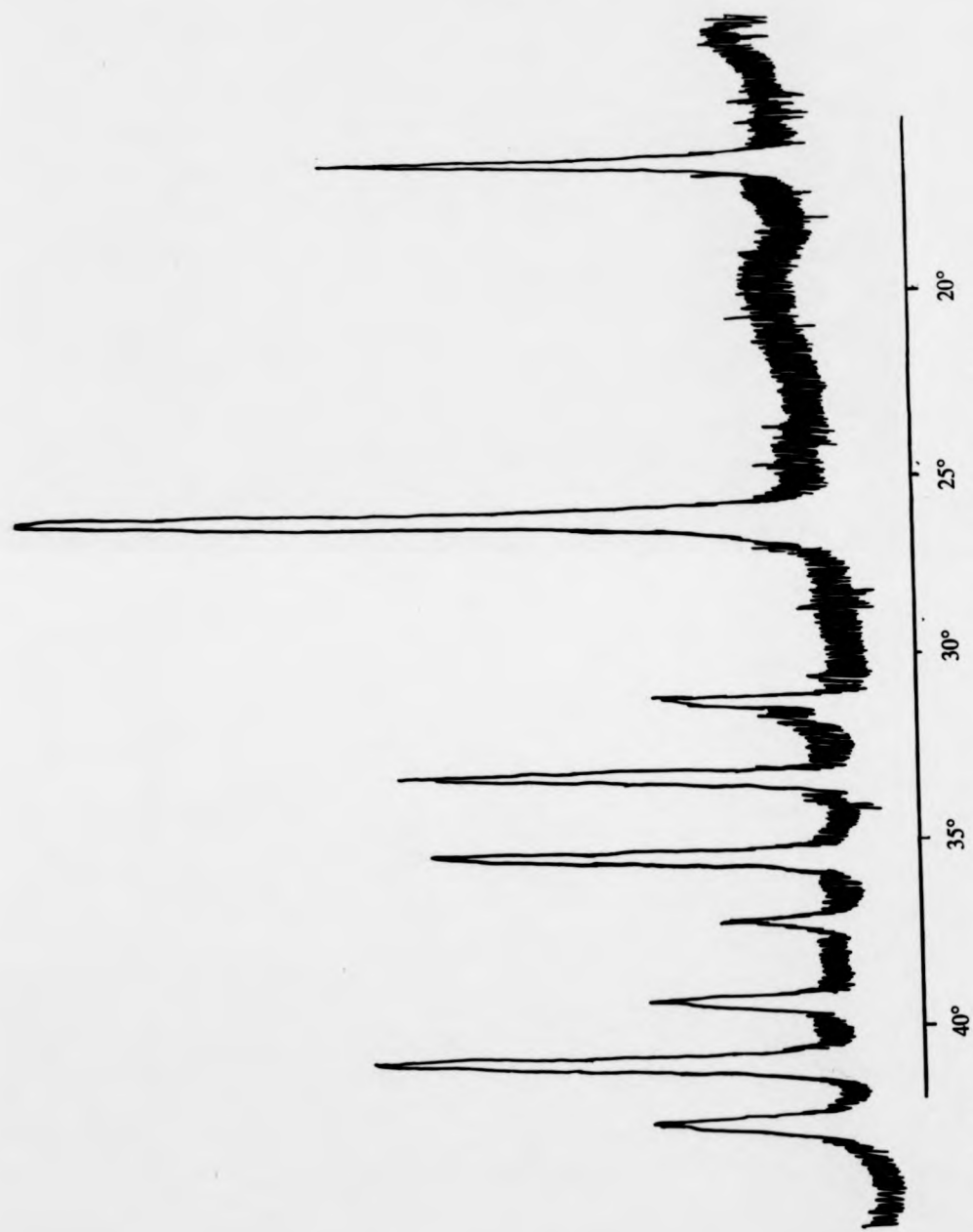


Figure 4.10) X-ray diffraction pattern of the gel derived material after

completion of the 980°C exotherm.

All peaks are due to mullite

4.3 Gelation studies

It was decided to use butan-1-ol as the solvent since it was found that aluminium isopropoxide dissolved more quickly in butan-1-ol than in propan-2-ol. Incorporating this modification into the method a solution was made, M(B)3/2E, and this became the basis for several gelation routes. During the preparation of this solution, once all the components were mixed, the reaction vessel was covered immediately with several layers of a clear plastic film, this was to minimise the exposure of the solution to atmospheric humidity.

4.3.1 Effect of exposed surface area

In order to examine the effect of the exposed surface area on the time of gelation of the solution and the nature of the materials produced, portions of equal volume of the base solution were poured into various containers. The exposed areas were 10.2 cm², 91.6cm², 141.0cm² and 254.5cm², these solutions were named M(B)3/2EI, M(B)3/2EII, M(B)3/2EIII and M(B)3/2EIV respectively.

Sample IV solidified the most rapidly in less than 6 hours. After approximately 3 hours a film had formed on the surface of the liquid. This film then grew until it covered the whole of the surface of the liquid and continued to grow in thickness until no free liquid remained. A film was also observed on sample II, no film was detected on samples I and III. Samples I, II and III solidified within 17 hours.

4.3.2 Acidic gelation

Using the base solution, acidic mixtures were made. M(B)3/2HI was taken to pH 3.9 by the addition of concentrated nitric acid. Using the same acid M(B)3/2HII was taken to pH 2. Sample HI gelled in under 22 hours to yield a clear, colourless gel. HII gelled in approximately 5 hours, this gel was translucent in appearance. Both samples gelled whilst being isolated from the atmosphere.

A portion of the gel HII was heated to 105°C, after 3 hours the gel had shrunk in volume and was surrounded by a supernatant liquid.

4.3.3 Parent solution

The base solution M(B)3/2E was stirred, whilst isolated from the atmosphere, for approximately 750 hours. After this period its appearance had changed from being translucent to being opaque. When this transition had taken place, stirring was stopped and the solution gelled within 24 hours. This material was named M(B)3/2J.

4.3.4 Gelation studies - Characterisation

4.3.4.1 Thermal analysis

The thermogravimetric behaviour of the materials M(B)3/2EIV and M(B)3/2HII was examined and taken as being representative of the other materials in their respective series. Both showed a rapid initial weight loss due to the removal of adsorbed water, this is followed by a more gradual loss that is attributable to the evaporation and combustion of the various organic compounds present in the gels. The overall weight loss of the HII gel was approximately 20%, EIV lost approximately 40% of its original weight over the temperature range used (20° - 1000°C), fig. 4.11.

Using the data from the thermogravimetric analyses the gels M(B)3/2HII, J and EIV were calcined at 800°C for 5 hours to remove all the residual organics. After this calcination the materials were shown to be amorphous to x-rays. These samples were then characterised using DTA techniques. All three materials exhibited a very sharp single exotherm at 980°C .

4.3.4.2 Infra-red studies

The supernatant liquid that was expelled from the gel HII on heating to 105°C was measured at pH1.

A solution of butan-1-ol and nitric acid was prepared to pH0, the infra-red spectrum of this solution was then taken, fig 4.12 (a). The spectrum of the supernatant liquid was also obtained, fig. 4.12 (b). The two spectra had peaks in identical positions, the only variation being slight intensity differences between certain peaks.

This suggests that the identity of the supernatant liquid is a mixture of alcohol, mainly butan-1-ol, nitric acid and water.

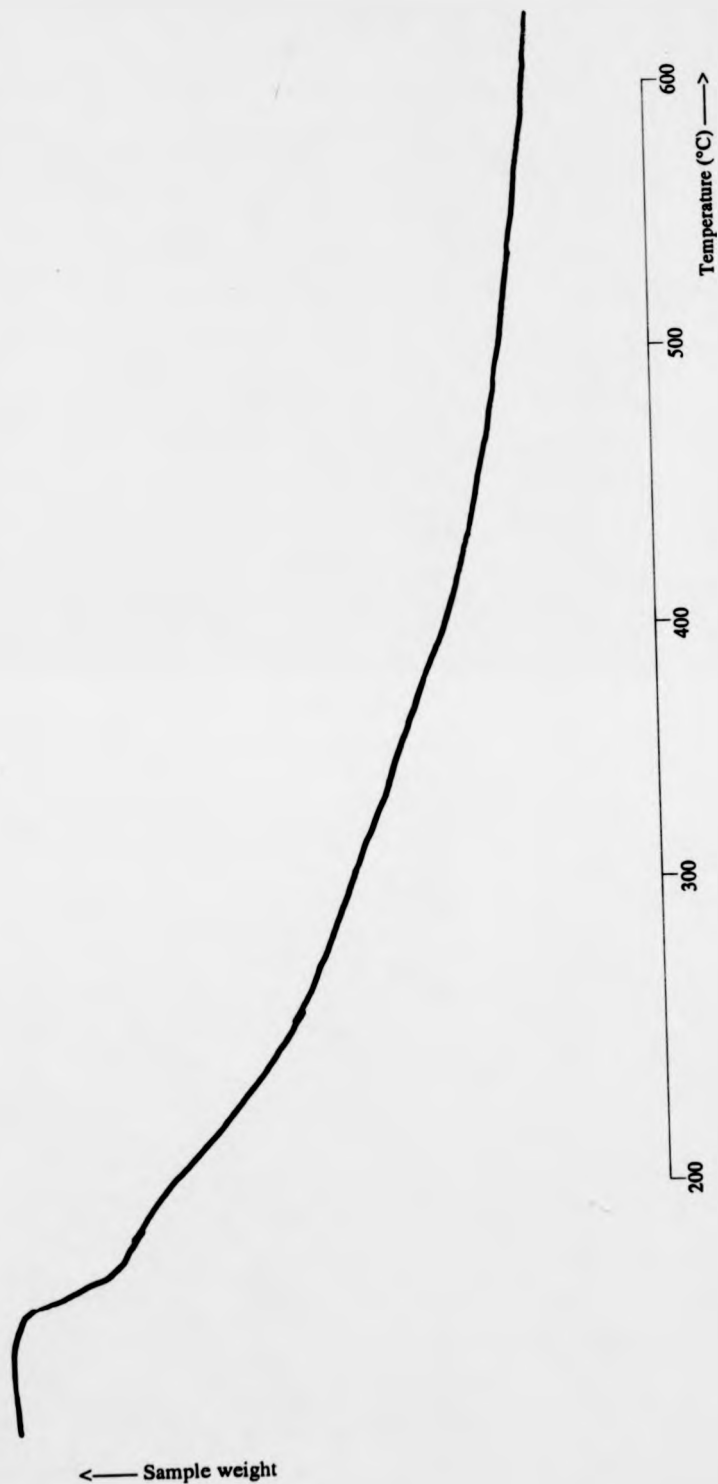


figure 4.11) Thermogravimetric behaviour of the sol deposition derived alcogel EIV.

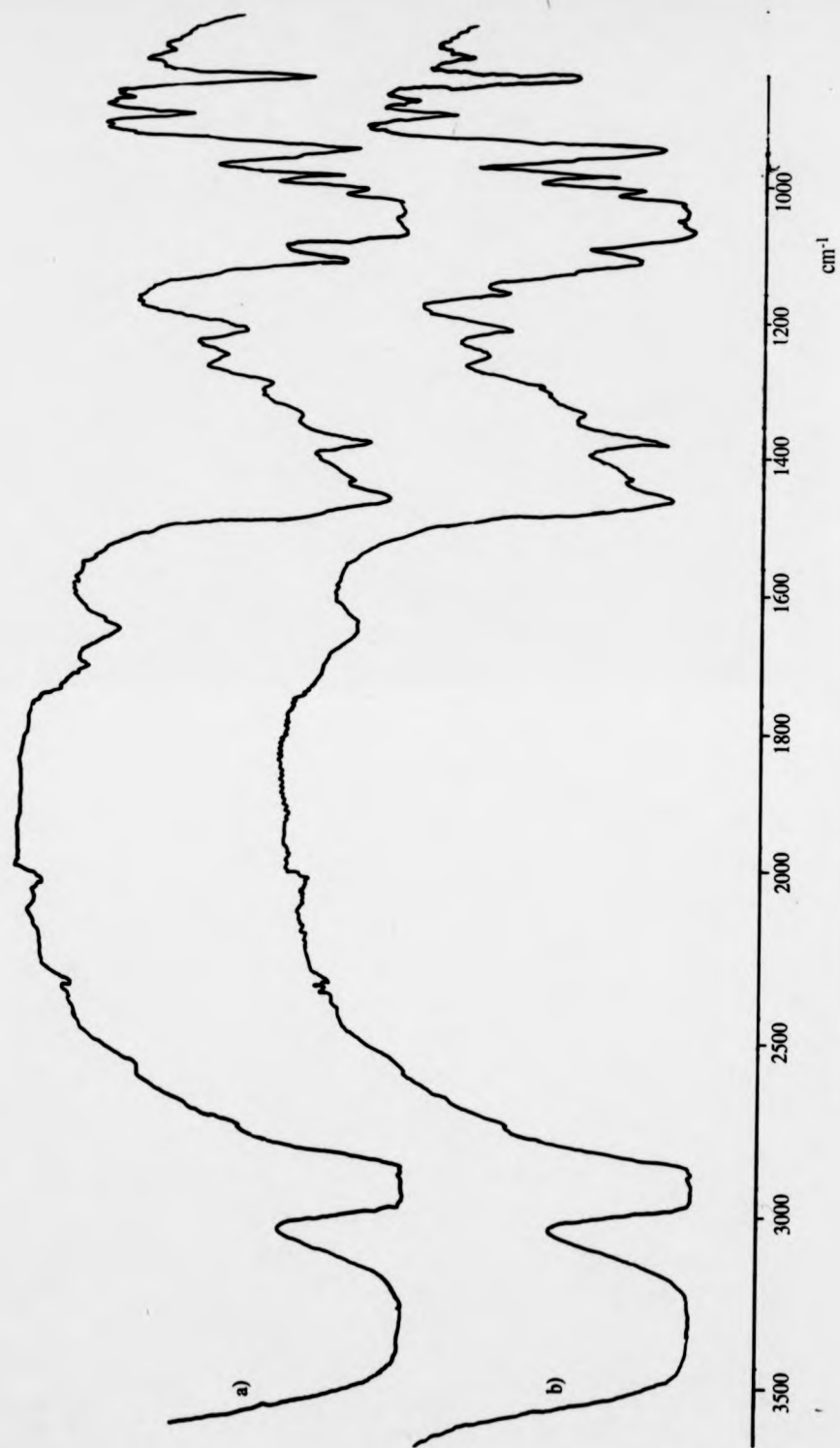


Figure 4.12) Infra-red transmittance spectra of a) a mixture of butan-1-ol and aqueous nitric acid taken to pH0, and b) the supernatant liquid from HII after heating at 100°C.

Table 4.1

M(B)3/2EII	M(B)3/2EIV	M(B)3/2HI	M(B)3/2HII	M(B)3/2J
	[20(21d)] A	[20(14d)] A	[20(14d)] A	
[190(48)] A	[450(66)] A			[250(72)] A
			[800(23)] A	
[900(60)] (M) & (U)	[850(90)] M		[850(90)] A	[850(90)] A
[990(1.25)] γ & M	[990(0)] M & (γ)		[990(0)] γ & (M)	[990(0)] γ & M
			[990(1)] γ & (U) & (M)	
[990(40)] M & (γ) & (U)		[990(20)] M & (γ) & (U)	[990(20)] (M) & (γ)	
			[1015(0)] γ & (M)	
[1080(19)] M & γ				
	[1100(24)] M & ((γ))		[1100(24)] M & γ	[1100(24)] M & (U) & (γ)

← Increasing Temperature (°C)

X-ray diffraction results of the gelation studies samples. Calcination conditions [Temp°C (hours or d(ays))]. Key:- A = Amorphous, M = Mullite, γ = the spinel phase and U = unidentified peak at 4.17 Å d-spacing. The phases are in order of strength of the diffracted peaks. Parentheses indicate weak reflections, double parentheses indicate very weak reflections. N.B. the samples with crystalline phases indicated were not necessarily fully crystalline.

4.3.4.3 Crystallisation patterns

Table 4.1 shows the crystalline phases present in various materials after various heat treatments. The x-ray diffraction results can be split into two categories, heat treatments below and above the 980°C exotherm. Calcinations above the exotherm shall be considered first, neglecting the unknown phase.

All gels except M(B)3/2EIV shows spinel as being the primary crystalline phase for short time calinations at 990°C. As the length of time at temperature increases the relative amounts of the spinel and mullite phases changes in favour of mullite.

Neglecting the unidentified phase at low temperature calcinations, all except the E-type materials show no evidence of any crystalline phases. The E-type materials become

partially crystalline after long periods at relatively low temperatures. the material EIV, in particular, shows quite a strongly crystalline x-ray diffraction pattern after 90 hours at 850°C, twelve peaks, all attributable to mullite, could be discerned.

The unidentified peak was only observed when glazed porcelain crucibles were used, although it was not always observed when a sample had been heated in such a crucible. Since this diffraction peak was never observed when alumina crucibles were used it was concluded that the crucibles were responsible for the phase that gave the peak. The possibilities are that either some species from the glaze diffused into the sample during the heat treatment causing the crystallisation of the phase, or the phase crystallised at the point of contact between the sample and the crucible.

To observe the effects of the type of crucible on the xerogel, two portions of the same xerogel were heated to 400°C (16 hours). They were then heated to 550°C, one sample was heated in an alumia crucible and held at 550°C for 20 hours, the other was in a Pt/Rh crucible, and was held at 550°C for 13 hours. X-ray diffraction of the resultant xerogels showed the sample heated in alumina to be amorphous, that heated in the Pt/Rh had traces of mullite.

This result confirms the decision to use alumina crucibles during all heating schedules.

4.3.4.4 Discussion

A range of materials were fabricated using various methods. The effect of increasing the surface area increases the amount of contact with atmospheric humidity. This water hydrolyses the metal organic species and the sol-gel process is then initiated. The largest exposed area that was used yielded the fastest gelling sample, this follows from a simple consideration of the amount of water available to a given volume of sample. In terms of the sol-gel reactions discussed in chapter 1, and within reasonable limits, the more water available to the system the more hydrolysis and condensation can take place and thus a network would be created more quickly. The samples fabricated using smaller exposed surface areas would also suffer from a minimum amount of diffusion of water from the atmosphere. The major source of water, particularly for the regions furthest away from the

surface, would be from water generating condensation reactions.

The nitric acid was of course in aqueous solution and this was the source of water. The solution with the lower pH gelled in the shorter time but had the more water added. If the nitric acid has any effect on the reactions occurring then it is probably as a catalyst. The effect of the pH can not be established from the experiments that were carried out.

This series of preparations has yielded a series of insights into the fabrication of mullite by sol-gel techniques. Slow hydrolysis by water from the atmosphere gives gels that crystallise to mullite as the major phase at 980°C. This is an important temperature for aluminosilicates, in particular for the mullite composition. As described earlier this temperature is invariant, the material may partially crystallise to mullite or to a cubic alumina rich phase. The phase that results on completion of this exotherm may be used to infer the overall composition and structural homogeneity of the material prior to crystallisation. If any significant segregation of the alumina and silica coordination polyhedra exists in the xerogel on heating, the first crystalline phases that should be seen will be alumina rich. Prior to crystallisation the material is amorphous, the silica rich regions of the material will be relatively stable since silica is a glass forming polyhedron according to Zachariasen [134]. Alumina is considered as an intermediate, that is alumina polyhedra may take place in a glassy network without disrupting the network but it cannot form a glassy network on its own. Based on these considerations and assuming a significant amount of segregation, an alumina phase would be expected to be the first that crystallises.

Should the network be homogenous, both in terms of the composition and the structure, the situation is of optimum mixing of the coordination polyhedra of alumina and silica. This may be envisaged as a mullite glass, possibly similar to that proposed by Morikawa *et al* [130]. The random and intimate mixing of the alumina and silica would promote the crystallisation of mullite, the only stable crystalline aluminosilicate phase under ambient conditions.

Thus the behaviour of the xerogel on heating, more specifically the phases that are yielded on devitrification, may be used to determine the homogeneity of the xerogel. This method is of course destructive and irreversible, it does however provide a very useful test

to model the structure of the amorphous xerogel. The absence of any general non-destructive and penetrative techniques that allow the structure of glasses, or highly disordered materials, to be elucidated further enhances the usefulness of this method. Since no other aluminosilicate phases are stable under the conditions used, this makes interpretation of the results obtained easier, a bonus for any technique.

The structure of the xerogel is a direct product of the fabrication procedure used in its production. An inhomogeneous xerogel is yielded when the hydrolysis and condensation reactions of the aluminium and silicon precursors are mismatched. That is when preferential reactions of one of these precursors occurs. Silicon alkoxides are well known for having relatively slow hydrolysis rates in comparison with the alkoxides of other metals, notably aluminium, titanium and zirconium. In the production of aluminosilicates this means that the addition of water to the system needs to be limited and slow, otherwise the aluminium alkoxide preferentially hydrolyses. The preferred condensation reactions are water liberating as opposed to alcohol liberating (see chapter 1). Thus condensation reactions between partially hydrolysed aluminium alkoxides will occur in preference to those between partially reacted aluminium species and unreacted silicon alkoxide species. This gives rise to the idea of self-polymerised species within the network, the building up of regions of inhomogeneity. Thus a fabrication procedure that allows the self-polymerisation of one of the precursor species will yield an inhomogeneous material. Heat treatment of this material will result in the crystallisation of the cubic alumina rich phase. Such a fabrication method may then be considered to be unsatisfactory as far as the aim of producing a material of maximum homogeneity is concerned.

On the basis of this consideration, the preparation methods used to produce these materials show a range of abilities. The acid catalysed gels gave rise to inhomogeneous materials. This can almost certainly be attributed to the fact that water was added directly to the alkoxide / alcohol solution. Even though only small amounts of water were involved, because of the direct addition method quite large gradients in the local water concentration will have been temporarily established. The regions of high water concentration consequently gave rise to the self-polymerisation of the aluminium *isopropoxide*. The slow addition of water from the atmosphere gave rise to materials of significantly greater

homogeneity. The gel M(B)3/2J was shown to be relatively inhomogenous but gives rise to some very interesting questions. Why was a gel formed when no water was deliberately added to the solution? Possibly a more pertinent point is that the solution that eventually gelled was the base solution. The reagents used were of >95% purity and water was removed from the alcohol by an aluminosilicate molecular sieve, and although care was taken to minimise the amount of water able to contaminate the solution, the ultra-dry conditions needed for total water removal were not used. On the basis of this some hydrolysis of the alkoxides should be expected. It was this solution that was used as the source of material for the other fabrication routes that gave xerogels of a range of homogeneities. Any reactions that were occurring in the base solution were swamped by the effect of hydrolysis from atmospheric moisture and water from the nitric acid solution. Thus the reactions occurring in the base solution were very slow, this would appear to rule out any significant amount of hydrolysis and condensation especially when it is considered that the net polycondensation reactions consume water.

The behaviour of the base solution on stirring for a long time therefore, would appear to be governed by reactions which are not strictly described by the basic sol-gel equations given in chapter 1 (specifically eqns. 1.1 -> 1.4).

4.4 Sol deposition method

Based on the results of the gelation studies the most homogeneous materials that were produced were those with a large exposed surface area (when the solution volume was taken into account). It was decided to use this technique as the basis for further fabrication development. In order to minimise contact of the solution with excess atmospheric moisture a flow of hot air across the solution was used. This flow causes the evaporation of the solvent, and any other volatile species present. A solid alcogel is deposited in a short time, the exact time being dependent on the air flow characteristics and the solution area / volume ratio. The conditions that were used allowed the solid to be formed within approximately 2 hours. This method is similar to that described by Iler [14], and is described by him as having several inherent technological advantages when compared with other sol-gel fabrication methods. The act of solvent removal means that

most of the organics are removed from the system whilst the solid is being deposited, and so shrinkage rates for the solid are considerably less than for bulk gel samples. During the deposition the sols are of a range of sizes and efficiently pack together to leave a dense coating on the substrate / container.

4.4.1 Materials characterisation

The inference of the level of homogeneity of the xerogel by the relative amounts of the two crystalline phases, mullite and spinel, can be used to characterise the materials produced by various fabrication methods. The important parameter that must be considered is that the materials should undergo a standard heat treatment schedule, this will allow the direct comparison between materials of different fabrication routes. The initial method chosen was to heat the xerogels to 1010°C in a muffle furnace, ramping to this temperature at 5°C/min and dwelling for 10 minutes. There exists however a significant variation in temperature across the furnace, estimated at about 30°C at the temperature of concern. The potential variability that this might bring about in the crystallinity of samples (as several samples were loaded into the furnace at once) was considered too great as to allow any meaningful comparison. This method was consequently only used for one series of samples. The more reproducible method that was decided upon was to heat the samples in thermal analysis equipment until completion of the 980°C exotherm (taken as 995°C).

The partially crystallised materials were then analysed using x-ray diffraction. The diffraction patterns showed a mixture of three phases, one amorphous and two crystalline phases. In order to express the relative degree of mullitization in a semi-quantitative manner, the peak heights of two diffraction maxima were measured. The ratio of the two values then defined a dimensionless number that was named the homogeneity coefficient. The diffraction maxima used were the reflections from the (110) planes of mullite (occurring at 2.525Å) and the reflection from the (440) plane of the spinel phase (occurring at 1.977Å). These particular peaks were chosen because this spinel reflection is the most intense, and there is no mullite peak at 1.977Å, hence no deconvolution is necessary. The mullite peak occurs at approximately 61° (2θ) and the spinel peak at 67° (2θ), i.e. relatively close to each other, minimising any instrumental effect, such as

broadening. The ratio that was used was;

$$\text{Homogeneity coefficient} = \frac{\text{Peak height of the mullite reflection}}{\text{Peak height of the spinel reflection}} = \frac{P_{m(110)}}{P_{s(440)}}$$

This coefficient gives a guide to the relative amounts of spinel and mullite and hence the original homogeneity of the xerogel. It does not give a measure of the overall degree of crystallinity of the glass ceramic.

4.4.2 Results

The variation in the homogeneity of the xerogels with the period of stirring of the solution is given in fig 4.13. A relatively dilute solution was used with 0.083M TEOS and 0.25M $\text{Al}(\text{OPr}^i)_3$ in the alcohol. At low stirring times mainly spinel is yielded. Up to a period of 13.5 hours stirring no detectable mullite was observed. At very long stirring times, >45 hours, mainly spinel was produced, although it appears that some mullite is always present. For stirring times intermediate between these two a significant amount of mullite was yielded, this leads to the peak on the curve of fig. 4.13.

4.4.3 Series E.A. and E.C.

Using the standard conditions and materials, two solutions of 0.5M $\text{Al}(\text{OPr}^i)_3$ and 0.167M TEOS in butan-1-ol was prepared. The precursors which had been stored under nitrogen were weighed out in air, added to the alcohol and transferred to a nitrogen cabinet. They were in contact with air for less than five minutes. In the nitrogen cabinet the container was sealed and the solution was stirred, the isopropoxide was dissolved in the alcohol overnight prior to the addition of the TEOS. Aliquots of the solutions were taken at various time intervals and transferred to flat bottomed petri dishes to a depth of approximately 1mm. These dishes were then placed in a drying oven at a temperature of 120°C and the formation of a dry alcogel took place within 2 hours. The burnout and thermal analysis calcinations were carried out in corundum crucibles.

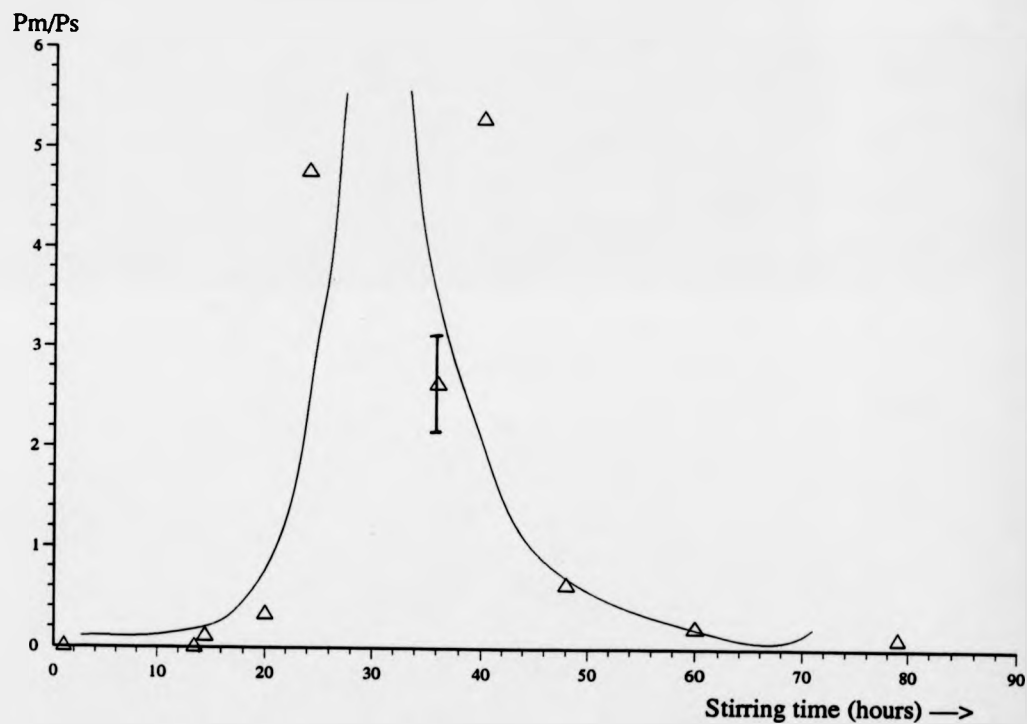


Figure 4.13) Variation in the homogeneity coefficient with stirring time for the initial sol deposition series

4.4.4 Series tanw

The standard method was followed using 2-methylbutan-2-ol (tertiary amyl alcohol) as the solvent. This was done to examine the effect of a very bulky alcohol on the homogeneity - time characteristics. This alcohol has a similar boiling point to butan-1-ol, this was an important factor in its choice since the rate of removal of the volatiles may have an important effect on any hydrolysis of the sols during the drying procedure.

4.4.5 F-Series

The standard method was followed, however a small amount of water was deliberately added to the system at the same stage as the TEOS was added. Using the parameter R, which is the simple ratio of the number of moles of water in comparison with the number of moles of alkoxide, the quantities involved gave a value of 0.11. Although useful for single component systems, this parameter gives little help in visualising the situation in a multicomponent system. Possibly a more useful term is the direct ratio of the number of deliberately added water molecules, and the number of M- OR bonds,

$$\text{i.e.} \quad [\text{Al}(\text{OPr}^i)_3] = 0.500\text{M}$$

$$[\text{Si}(\text{OEt})_4] = 0.1670\text{M}$$

for a solution of 300cm^3

$$\text{the number of moles of } \text{Al}(\text{OPr}^i)_3 = 0.15$$

$$\text{the number of moles of } \text{Si}(\text{OEt})_4 = 0.05$$

$$\text{the number of moles of water} = 0.022$$

$$\begin{aligned} \text{Thus the total number of M- OR bonds is } \{ (0.15 \times 3 + (0.05 \times 4)) \} \\ = 0.65 \end{aligned}$$

$$\text{Thus the direct ratio of } \text{H}_2\text{O} / \text{M- OR} = 0.034$$

$$\text{i.e. } 29.5 \text{ M- OR bonds per molecule of water.}$$

4.4.6 Results and discussion of homogeneity variation with time

The variations in the homogeneity coefficient of the sol series E.A. & E.C., tanw, F and H with the period of stirring are presented in figs. 4.14 -> 4.17 respectively, the lines are drawn on the figures to guide the eye. The data from the series E.A. and E.C. have been combined as the conditions used during the preparation and fabrication were identical, within experimental error. E.C. was a more detailed map of the region of interest, -20 hours stirring.

The pattern of the variation in homogeneity with the stirring time found for the various routes used here were similar. Similarity to the behaviour of previous preparations was also noted. This is an important result, it shows that whatever reactions are taking place, the behaviour of the solutions is reproducible. That is at low stirring times the material produced after drying is inhomogeneous, continued stirring then produces an increase in the level of homogeneity. The homogeneity coefficient then goes through a maximum and then decreases.

The addition of a very small amount of water to the system does not appear to have significant effect on the behaviour of the system.

That a variation in the level of homogeneity occurs between samples of the same preparation, indicates that some form of reaction is occurring and that any hydrolysis-condensation type reactions are not simply due to contamination of the precursors by water. It may be assumed that any contamination occurring to either the precursors, or to the solution as a whole, would have approximately the same effect on all samples in that particular preparation. For example, if we consider the samples being contaminated by water from the atmosphere during the alcohol removal stage of the process. All the samples are of approximately the same surface area /volume and no significant differences in the time to gel between samples within any particular preparation was detected. Therefore the samples were exposed to a similar amount of atmospheric water whilst in the liquid phase. These samples may then be expected to undergo a similar degree of reaction with the water to which they were exposed.

Thus we may assume that if all the reactions that occur are due to water, from contamination of either the precursors or during the process to obtain the material, samples

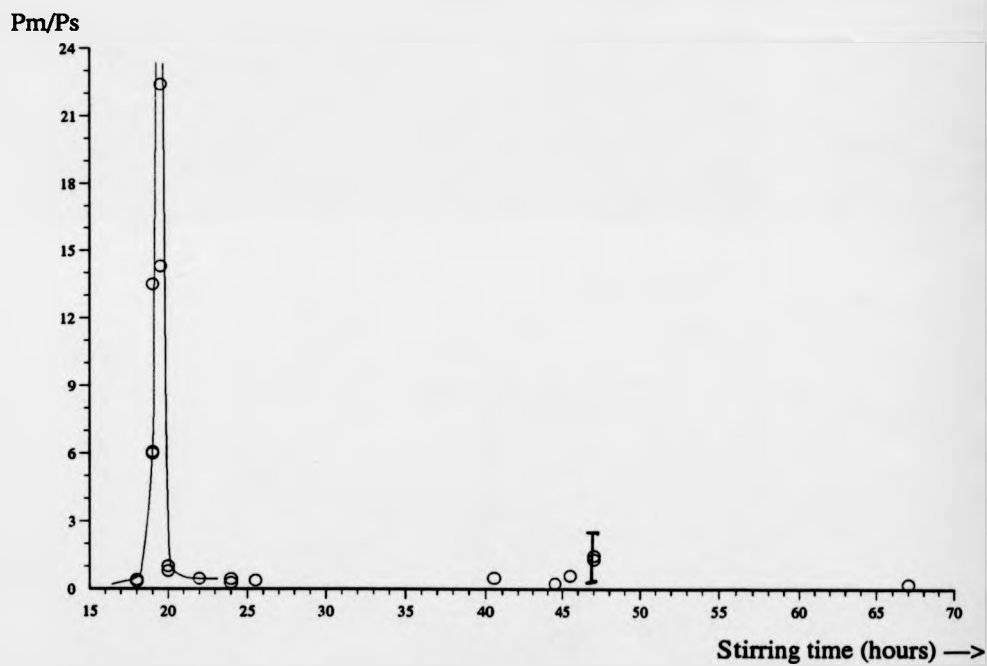


Figure 4.14) The variation in the homogeneity coefficient with the stirring time of the E.A. & E.C. series of gels.

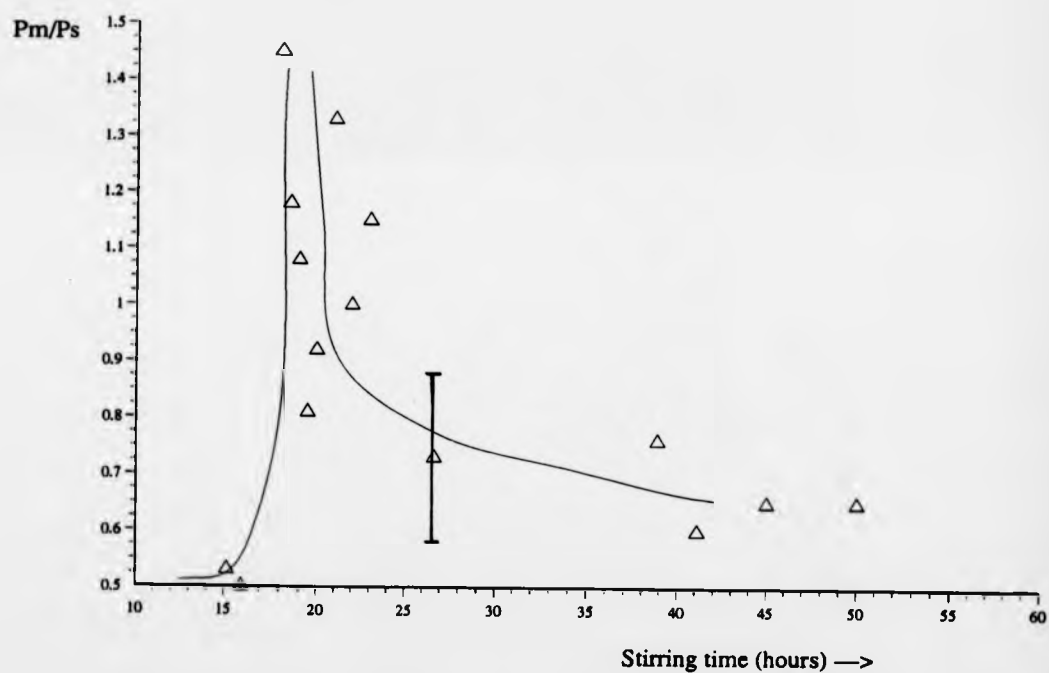


Figure 4.15) The variation in the homogeneity coefficient with the stirring time for the tanw series of gels.

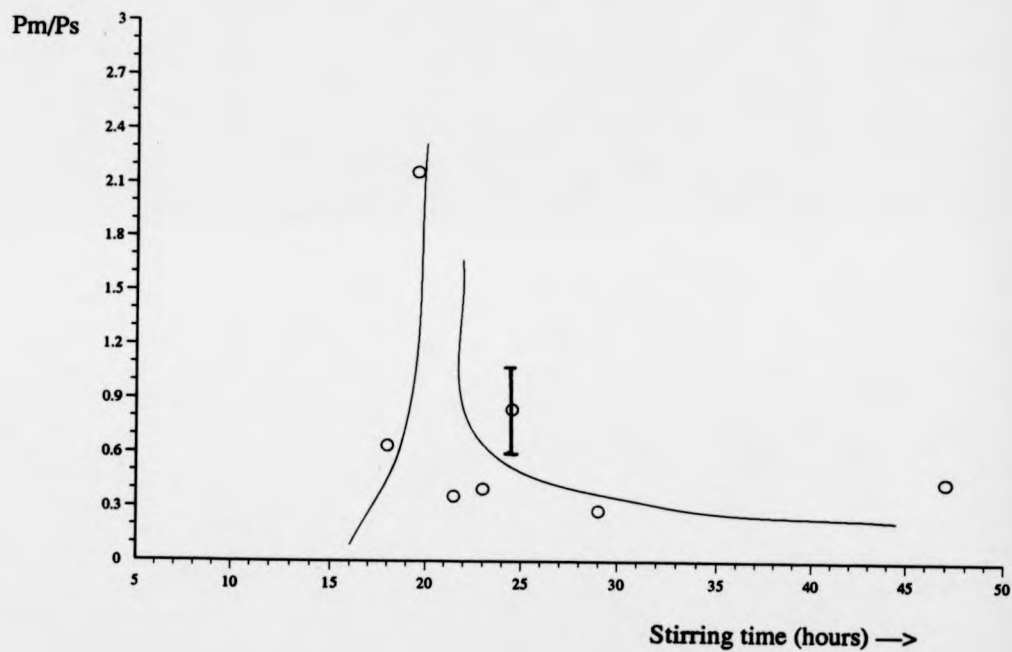


Figure 4.16) The variation in the homogeneity coefficient with the stirring time for the F series gels

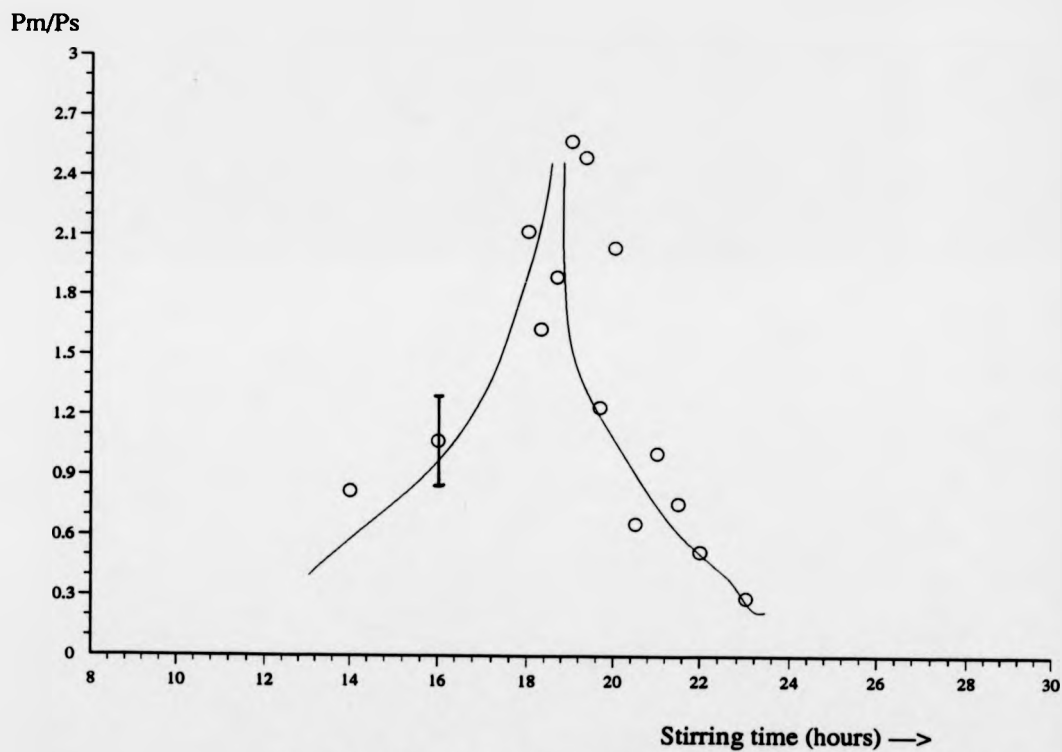


Figure 4.17) The variation in the homogeneity coefficient with the stirring time for the H series of gels.

of similar levels of contamination would be expected. This would manifest itself as a random variation in the level of homogeneity with the variation in the stirring time. A regular variation in the level of homogeneity within a series of samples formed from the same parent solution would not be expected. The reproducible nature of these variations in the homogeneity, with the length of time of stirring of the base solution, also tends to rule out specific contamination of particular samples within each series.

The fact that powders are yielded on very low temperature heat treatments informs us that sols are being produced in the parent solution. That mullite, to a greater or lesser extent, is nearly always produced on heating to 980°C tells us that Al-O-Si bonds have been formed. Since there is a regular variation in the homogeneity of the samples with the time of stirring to which the parent solution was subjected, we can conclude that some type of reaction is taking place within the parent solution. The nature of these reactions are unidentified by the experiments carried out. There is no doubt that a small amount of water is present in the system, but not enough to explain these observations in terms of the traditional sol-gel reaction, especially when it is considered that these reactions demand a net water consumption. The explanation for the condensation reactions that are undoubtedly taking place must be sought elsewhere.

The maximum homogeneity of the gel appears to occur after about 18-19 hours stirring of the parent solution. This regular variation in the homogeneity immediately suggests that some time dependent reaction between the precursors is occurring. The reproducibility of the behaviour suggests that contamination of the solutions is unlikely to be responsible for the behaviour. A similar pattern is observed when a bulkier alcohol is used, the time at which the maximum homogeneity occurs is identical to that observed when 1-butanol is used. The generally accepted role of the alcohol in the sol-gel reactions is as a precursor modifier via organic, or alcohol exchange. The bulkier the alcohol the larger the steric hindrance to the reaction taking place. If the organic exchange played any significant determining role in the condensation reactions occurring, any steric effects would be expected to show up in the rate at which the reactions occurred. The fact that the time of stirring to yield the maximum homogeneity is the same for the two alcohols used would appear to indicate that the nature of the alcohol does not play a central role in whatever condensation reactions are occurring.

4.4.7 Spray Drying

The standard preparation procedure was followed to make up a solution, series X. Five samples were removed from the solution after 24, 26, 30, 44 & 55 hours reaction time. The sols were deposited in the previously described method except for the first sample. The portion of solution that was removed after 24 hours was placed in a spray gun arrangement. Using pressurised air as the propellant the liquid was sprayed into a heated aluminium sphere. The sphere was heated in order to vapourise the organics in the spray so a deposit of the sols would be left. The deposit was collected and characterised according to the established technique. The spray dried material yielded the 980°C exotherm, with both mullite and spinel being yielded. On the basis of this simple comparison with the other materials fabricated as part of this series, the spray dried alcogel showed no significant variation that might suggest that spray drying methods may be intrinsically unsuitable in the fabrication of mullite alcogels.

4.5 Alcohol effects

In order to investigate the effect of alcohols on an alkoxide, a series of experiments were carried out using aluminium *sec*butoxide, this compound was chosen for its reactivity. A range of alcohols were placed in sealed containers, containing dry aluminosilicate molecular sieve, and left for several days. Under a nitrogen atmosphere approximately 1cm³ of each dry alcohol was poured into separate bottles containing fresh aluminium *sec*butoxide. As a control the alkoxide was also added to a similar volume of distilled water. The alkoxide was used as received, it was opened and stored under nitrogen. Table 4.2 shows the results of these simple tests.

These results give a consistent, if surprising, trend. Primary alcohols cause the aluminium alkoxide to form a gel and the fact that the secondary alcohols do not, suggests that steric effects are important in the reactions occurring. In order to further investigate these effects several samples were studied using static ²⁷Al NMR techniques.

Solvent	Comments
Methanol	A gel was formed immediately on mixing
Ethanol	A gel was formed on shaking
Propan-1-ol	A gel was formed on shaking
Propan-2-ol	A clear colourless solution was formed
Butan-1-ol	A gel was formed on shaking
Octan-1-ol	A gel was formed on shaking
Hexan-1-ol	A gel was formed on shaking
2-methylbutan-2-ol	A clear colourless solution was formed
Water	A gel was formed immediately on mixing

Table 4.2
Effect of adding aluminium *secbutoxide* to a range of common solvents.

4.5.1 ^{27}Al NMR - results

The spectra of the various gels and liquids are given in fig. 4.18-> 4.22. The signals were processed using only Fourier transformation, no smoothing or line broadening factors were used. The aluminium *secbutoxide* itself was analysed by NMR, and the spectrum of this viscous liquid is given in fig 4.18. It can be seen that a very broad spectrum, centred around approximately 0ppm was obtained. A more definite peak centred around 2.5ppm was superimposed on this broad background. Both these signals correspond to octahedral aluminium. The poor signal to noise of this spectrum indicates that there is a small amount of aluminium in the well defined octahedral environment compared with the aluminium in ill defined octahedral coordination. The gel that was formed by adding the alkoxide to water gives a very broad, large peak centred at about 8ppm, fig. 4.19. The spectrum is ill-resolved due to the fact that the resonance was taken statically with no averaging of the anisotropic broadening mechanisms. We can conclude that the effect of water is to promote the existence of octahedrally coordinated aluminium. The small octahedral peak observed in the alkoxide alone can be assumed to be caused by water from the atmosphere since the rotor was packed and the NMR experiment was run in air. Fig 4.20 shows the spectrum of the gel formed when the alkoxide was added to butan-1-ol, a very sharp, single resonance was observed at 7ppm. The octahedrally coordinated aluminium in this material was in a very well defined environment. There also exists a very broad, very weak resonance



Figure 4.18) The ^{27}Al NMR spectrum of $\text{Al}(\text{OBu}^t)_3$.



Figure 4.19) The ^{27}Al NMR spectrum of the $\text{Al}(\text{OBu}^t)_3$ - water gel.

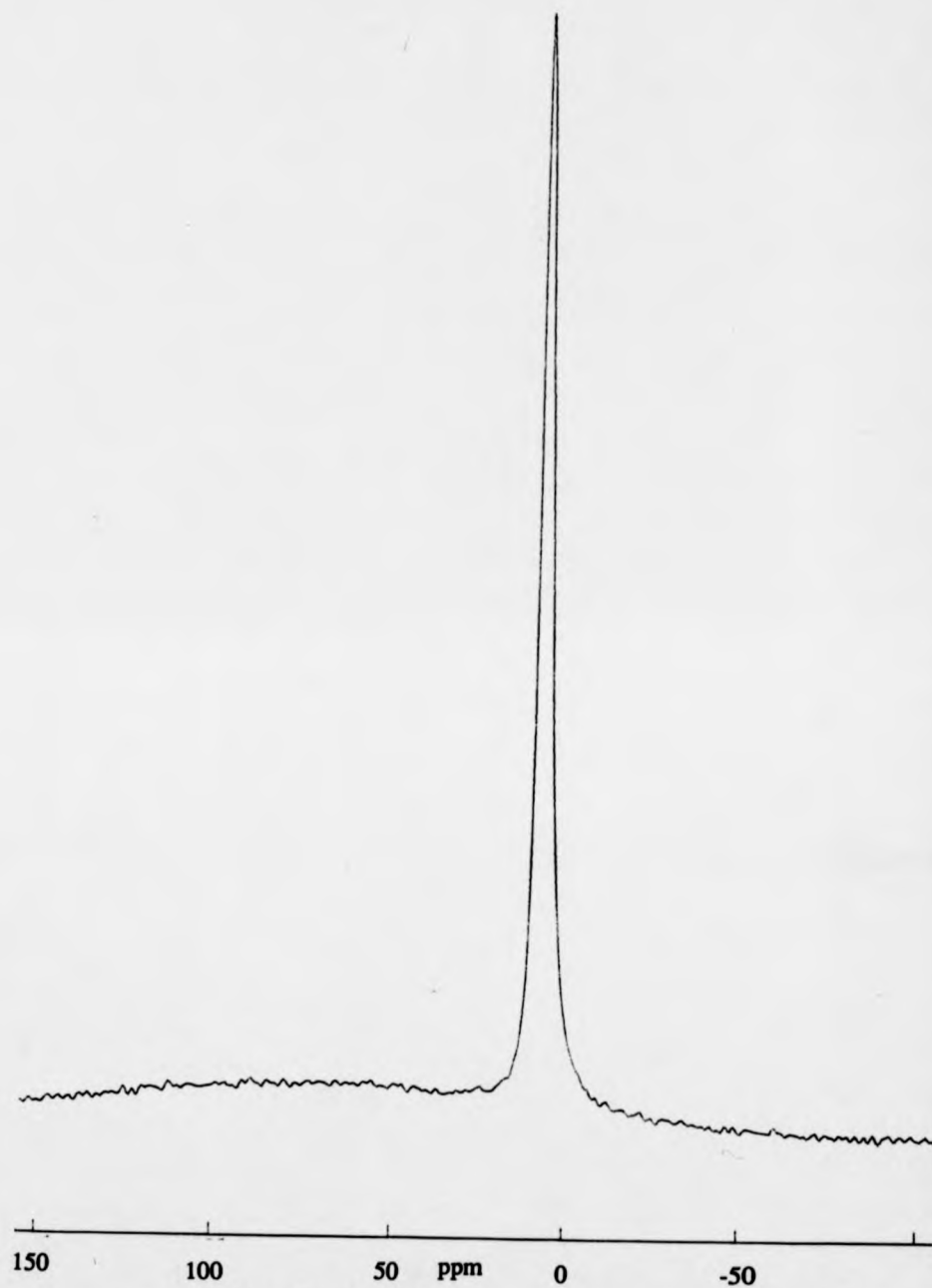


Figure 4.20) The ^{27}Al NMR spectrum of the $\text{Al}(\text{OBu}^*)_3$ - 1-BuOH gel.

centred at approximately 60ppm, probably corresponding to tetrahedral coordination. The solution of the alkoxide in propan-2-ol also gives two strong peaks. The octahedral resonance is sharp and centred at about 3.5ppm, the tetrahedral peak, ~50ppm, is very strong and very broad, fig. 4.21. The solution of tertiary amyl alcohol and the alkoxide shows aluminium in tetrahedral environments, though possibly a small amount of octahedral aluminium also exists, fig. 4.22.

4.5.2 Discussion

The presence of water causes the aluminium *sec*butoxide to condense according to the general sol-gel reactions. The aluminium preferentially enters a well defined octahedral environment, this is due to the building up of sols. More interestingly however is the effect of alcohols on this alkoxide. The primary alcohol gives a gel which has octahedral aluminium as the dominant coordination, although a small amount of tetrahedral is possible. The two secondary alcohols show tetrahedral aluminium as the preferred coordination with the amount of octahedral aluminium decreasing with the increasing bulkiness of the alcohol. The reactions which cause gelation when the alkoxide is added to the primary alcohols also occurs but to a greatly reduced extent when secondary alcohols are used, and even less when tertiary alcohols are used. The greater the ramification of the alcohols the less the reaction is occurring, as evidenced by the smaller amount of octahedral aluminium. These results indicate that steric effects dominate the reactions occurring. That the very small alcohols caused gelation on contact, and the larger primary alcohols needed agitation to cause the alkoxide to gel support this. The aluminium in the gel prefers an octahedral environment, whilst in solution it prefers tetrahedral coordination.

More important than the results in themselves though, is the implication that the alcohol does have an effect on the alkoxide, indeed the alcohol may cause the alkoxide to gel on its own.



Figure 4.21) The ^{27}Al NMR spectrum of the $\text{Al}(\text{OBu}^s)_3$ - 2-PrOH solution.

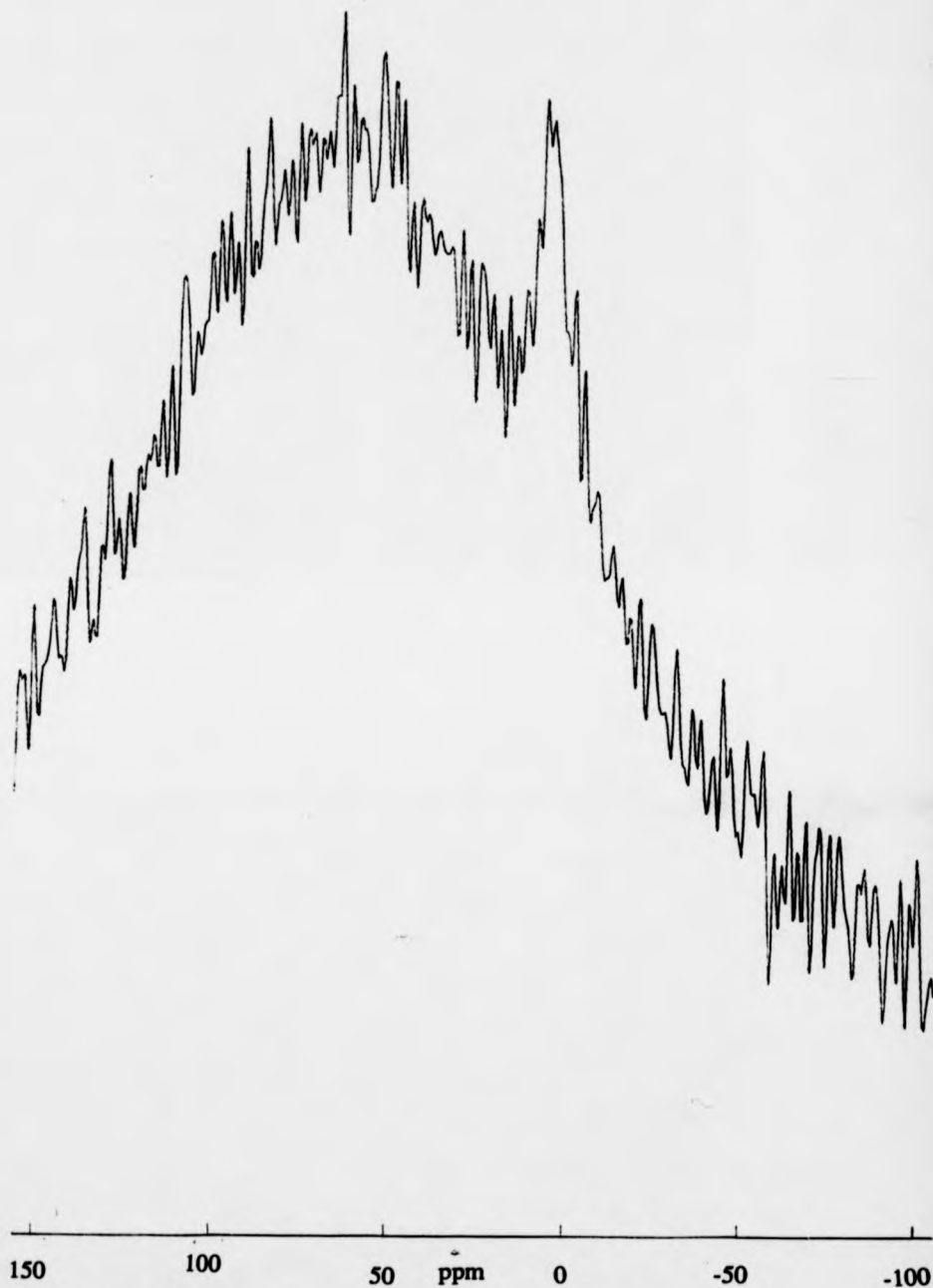


figure 4.22) The ^{27}Al NMR spectrum of $\text{Al}(\text{OBu}^s)_3$ - Am^tOH solution.

4.6 Densification

Sample	Density (g/cm ³)	Relative density	Comments
M(B)3/2EII 900°C (60hrs)	2.59	81.8	Partially crystalline mullite and cristobalite
M(B)3/2EII 1080°C (19hrs)	2.60	82.0	Highly crystalline, mullite and spinel
M(B)3/2HII 800°C (0.5hrs)	2.47	77.8	Amorphous
M(B)3/2HII 800°C (2hrs)	2.61	82.3	Amorphous
M(B)3/2HII 800°C (23hrs)	2.62	82.6	Amorphous

Table 4.3

The density and crystalline status of various materials after a range of heat treatments.

Table 4.3 shows the data of pressureless sintering tests carried out on the materials M(B)3/2EII and M(B)3/2HII. The xerogels were uniaxially cold pressed prior to sintering. The two M(B)3/2EII pellets were found to be partially crystalline after the heat treatment. The acid catalysed gels showed no evidence of crystalline phases after the various relatively low temperature heat treatments to which they were subjected. The maximum density that was achieved with this series of tests was approximately 82% of the theoretical density of crystalline mullite (3.17gcm⁻³).

In order to further study the limits that could be achieved by pressureless sintering several materials were fabricated.

4.6.1 Samples AA

An alcogel was prepared by the usual sol deposition method, with stirring of the solution being carried out for a few days. Approximately 0.5g of the alcogel was placed in a beaker with 100cm³ of distilled water, this mixture was stirred for 4 days and then placed in a drying oven at 95°C for 3 days. The resultant powder was ground using an agate mortar and pestle then cold uniaxially pressed into a disc of approximately 2.5cm diameter. Pressing was carried out until the disc could be moved without losing any of its integrity. The disc was then broken into two, the pieces were placed in alumina crucibles

and heated to 800°C at a rate of 10°C/hour, and then held at temperature for 5 hours. After this treatment one half of the disc (sample AA1) was removed, the other was left at 800°C for a further 5 hours (sample AA2).

4.6.2 Samples E.C.

Solution E.C. had been prepared for the homogeneity tests (section 4.2.4.4), after 23 days of stirring a portion was taken and used in these density tests.

Distilled water was added to the solution and the amount of water was equivalent to 1mole of water to two moles of M-(OR) bonds for the precursors. This assumes that the precursors were unchanged from their original form. This is inconsistent with the results of the homogeneity study but, if the precursors are assumed to have formed linear polymeric species, then the water added was sufficient to replace all the organics lining the inorganic backbone. After the addition of the water the solution was stirred for 21 hours. The sols were then deposited at 110°C, the powder ground and pressed into a pellet in the same manner as for sample AA. The disc was broken into two pieces and heat treated as follows.

ECW1AI

120°C (9 days)

250°C (3.5 hours)

800°C (5 hours)

ECW1AII

120°C (9 days)

250°C (24 hours)

400°C (24 hours)

600°C (24 hours)

800°C (24 hours)

It can be seen from table 4.4 that there is a significant difference between the skeletal and bulk densities obtained, with the skeletal densities always being significant greater. The skeletal densities that were obtained indicate that the theoretical can be achieved. That the bulk values are so much lower suggests that for a large sample this may be difficult. The high skeletal density suggests that the sols are dense. The increase in skeletal density between samples AA disc 1 and AA disc 2, and ECW1AI and ECW1AII respectively cannot be put down to a condensation mechanism as in mechanism II of Brinker and Scherer [12] (see section 1.6). All these materials have spent at least 5 hours at 800°C, the

Table 4.4

Sample	Bulk density (g/cm ³)	(ρ/ρ_a)	Skeletal density (g/cm ³)	(ρ/ρ_a)
AA Disc 1	1.45	0.49	2.27	0.77
AA Disc 2	2.41	0.81	2.95	1.00
ECW1AI	2.23	0.75	2.67	0.90
ECW1AII	2.51	0.85	2.86	0.97

The bulk and skeletal densities of various pressureless sintered samples. the value ρ/ρ_a is the ratio between the measured density and the theoretical density of mullite glass (2.96 g/cm³) [130].

more dense spent considerably longer at this temperature. Very few organic or hydroxyl groups will be left after this heat treatment, as evidenced by the thermogravimetric traces earlier in this chapter, thus little condensation could occur. Other explanations for the increase in density may be the collapse of micropores by structural relaxation or a small amount of viscous sintering. Both these mechanisms are consistent with the trend of increased density for long time heating. It must be noted however, that the glass transition of mullite stoichiometry gels has not been observed during this study, and to the author's knowledge has not been reported in the literature. This would appear to rule against the mechanism being viscous sintering.

4.6.3 Hot pressing

Two samples were heated to 900°C and then the pressure was applied. One sample was subjected to 65.0 MPa - the sample remained at temperature and under pressure for 3.5 hours. The recovered pellet was found to be x-ray amorphous and to have a density of approximately 2.55 g/cm³ (80.5 ρ/ρ_a). The second sample also had the pressure applied while it was at temperature, the pressure that was applied was 100 MPa and the sample was maintained under these conditions for 2 hours. This sample was also found to be x-ray amorphous and had a density of 2.71 g/cm³ (91.5 ρ/ρ_a).

4.6.4 Discussion

The attempts at densifying mullite stoichiometry xerogels have shown that it is possible to achieve 80% of the theoretical relatively easily. The remaining, and all important porosity becomes progressively more and more difficult to remove, it is almost a situation of diminishing returns. It has been shown by many workers in the field that densities of >95% can be routinely achieved at elevated temperatures (see chapter 2). This study set itself the aim of trying to achieve maximum density whilst keeping the material amorphous. Since the glass transition point has not been observed there can be very little, if any, viscous sintering. Incorporation of any fibres that are currently commercially available into a reasonably dense amorphous matrix would involve crushing the mullite powder around and into the fibres. This would obviously cause a lot of damage to the surface of the fibres reducing their effectiveness as reinforcement agents.

4.7 Chromatography

4.7.1 Gel permeation chromatography

The homogeneity variation with stirring time shows that condensation reactions are occurring. In order to try to identify, the condensation products, gel permeation chromatography was used.

A solution of aluminium *isobutoxide*, TEOS and butan-1-ol was made up as standard, the solution was stirred for approximately 19 hours and then passed through a 45 μ m filter. This was so a solution that contained reacted species was used but any very large species, unreacted precursor particles or debris that may damage the beads in the separating column would be removed. The solution was translucent and white in colour prior to filtering and was diluted approximately 5:1 with toluene to protect the column gel and to minimise the amount of hydrogen bonding the column had with the alcohol, the filtrate was clear and colourless. Toluene was selected as the best of a range of column compatible organic solvents. The filtrate was then passed through the column. The column had been calibrated with a solution of polystyrene. Fig. 4.23 shows the spectrum of the analysed filtrate, the peaks were identified as being due to the precursors and the alcohol. The curious feature of this spectrum is that the retention time of the $\text{Al}(\text{OPr}^i)_3$ was significantly greater than that

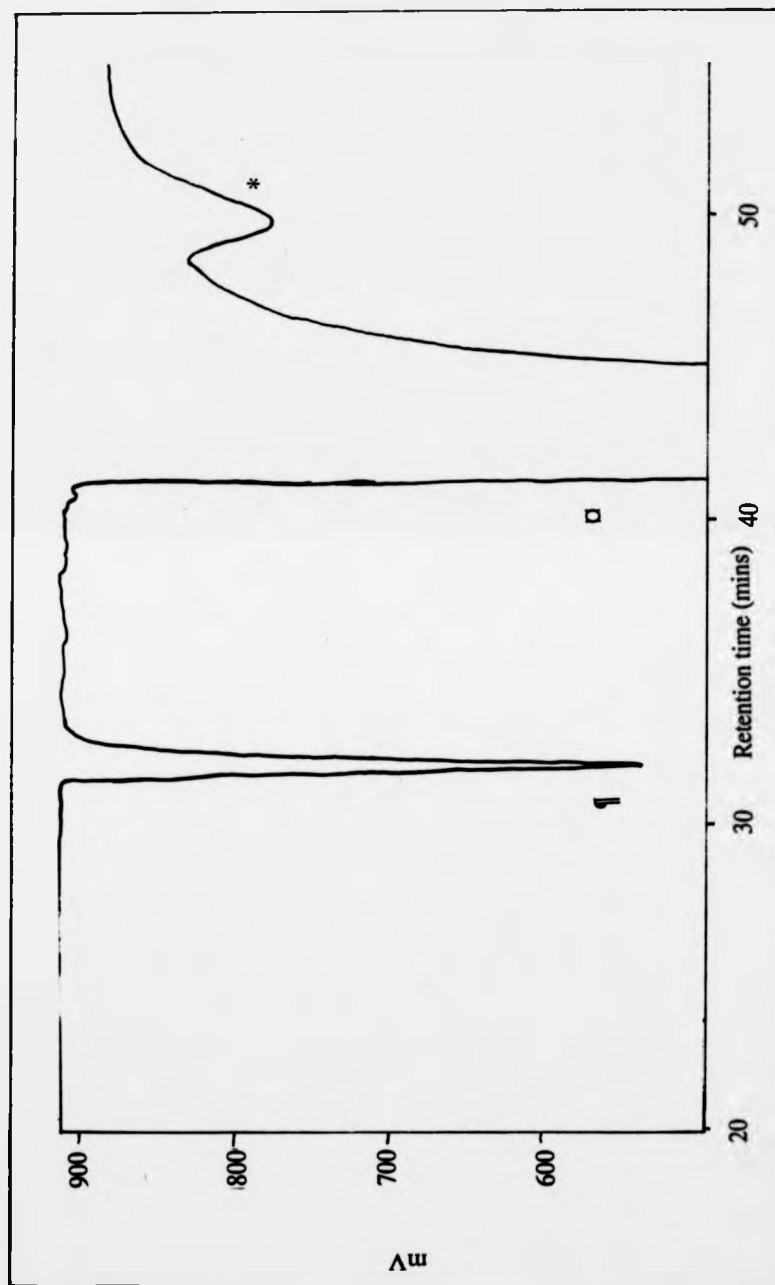


figure 4.23) Gel permeation spectra of mullite gel precursors, the peaks are due to;

- * Al(oPr)₃
- Butan-1-ol
- ¶ TEOS

of the TEOS, and was even greater than that of butan-1-ol. The molecular weight of the *isopropoxide* is 204.32, that of TEOS is 208.33. The *isopropoxide* is usually thought to exist in at least the dimeric form. From this consideration the retention time of this species would normally be expected to be shorter than the other reagents.

This technique is complicated by an interaction between the aluminum *isopropoxide* and the silicone based column gel. This may suggest that the polymeric species are shown on the spectrum but are in an unexpected place, possibly being masked. Alternatively, and more likely, the polymeric species were not detected. This may mean that the sols were not dissolved in the toluene or were removed by filtering, possibly the polymers remained in the column.

This technique was found to be inapplicable to the alkoxide / alcohol system used.

4.7.2 Gas chromatography - Mass spectrometry

In order to try and detect the polymeric species, or possible by-products of the condensation reactions, gas chromatography was used. A solution of aluminium *secbutoxide*, TEOS and isopropanol was made up under nitrogen to the standard concentrations. The *secbutoxide* was used because the solution had to be filtered for the same reason as for the GPC experiment. Since this alkoxide is liquid, and no precipitate was formed, it was reasoned that none of the precursor would be removed by this procedure. This solution was stirred for 18 days and then passed through the column. Both chemical and electron impact techniques were used. The species that were detected by the mass spectrometer included the precursors and the alcohol, and possibly a dimeric species. There was no evidence of any larger species.

There was however, a consistent detection of a species of mass 87 a.m.u., a possible explanation for this species may be that it is the breakdown product of Pr^iOEt . The data obtained is limited and no firm conclusions can be drawn from it at this point, although it may be speculated that this species is the by-product of a condensation reaction. In conjunction with section 4.5 it may be postulated that there is a reaction between the alkoxide and the alcohol giving rise to an activated aluminium species with the mixed ether being liberated. This activated species may then react with either passive or active alkoxides.

Chapter 5

Results:

The mechanism of crystallisation

5.1 Introduction

The crystallisation sequence of aluminosilicates has long been debated, see chapter 2, with the main controversy being centred around the exotherm at 980°C. There are several questions that are raised by this thermal event. Sometimes mullite is the only crystalline phase observed after the exotherm has occurred, at other times a cubic spinel phase is the only phase but often both phases are seen on completion of the exotherm. Why? The variation, in the relative amounts of these two phases, with the method of fabrication, as discussed in chapter 1, suggests that the level of homogeneity of the precursor material is the determining factor. This is in turn determined by the exact nature of the fabrication procedure. Thus for a very inhomogeneous gel where a significant amount of segregation of the the aluminium and silicon coordination polyhedra exists spinel is the major crystalline phase seen after the exotherm. An increased level of homogeneity in the precursor gel yields significantly more mullite. Although this summary is the generally accepted view of the situation, it allows little or no further insight into the mechanisms of crystallisation in these systems. In order to proceed further the problem needs to be approached from a different direction. If we accept that in some way the homogeneity determines the crystalline phases, and their relative amounts, yielded at 980°C we may then ask why is 980°C such an important temperature.

This question may be rearranged into a more useful form, "Why at 980°C is there the appearance of two different crystalline phases in these systems?" There is no *a priori* reason why these two phases should not crystallise independently at the same temperature, but there exists the possibility of a common cause. It is this common cause that will provide the focus of the results to be discussed on the crystallisation sequence of aluminosilicate xerogels.

5.2 Low temperature structure

Since the dominant factor in the behaviour of these materials appears to be their homogeneity, the low temperature structure and behaviour of these materials should yield some information that is useful in the elucidation of the mechanisms behind the 980°C exotherm. In particular the most valuable route should be the difference in the structure of materials that produce mullite and those that produce spinel.

5.2.1 Aluminium environments

The frequencies at which the aluminium nucleus resonates when excited by a pulse of frequency of 93.83MHz depend on the local environment. Octahedral and tetrahedrally coordinated aluminium are well characterised and resonate at chemical shifts of approximately 0 and 50 ppm with respect to AlCl_3 . These values are only very approximate guides since the local electric field which determines the exact frequency of the resonance depend on the nature of the species which surround the aluminium. For example, aluminium tetrahedra can give rise to resonances with chemical shifts between approximately 80ppm for $\text{Al}(\text{OH})_4$ and 51ppm $\text{Q}^4(4\text{Si})$ in zeolites. The existence of pentahedral aluminium and the frequency at which its resonance is observed is less well characterised. The first claimed observation of this coordination was in 1985 by Dupree et al [131] working with anodically formed amorphous alumina. Their assignment of the resonance at -30ppm as being due to pentacoordinated aluminium has been generally accepted and other workers have also observed this resonance [87,114]. Selvaraj et al [126] have proposed a structure for the pentacoordinated aluminate dimer formed from two trigonal bipyramids sharing an edge.

5.2.2 Non-stoichiometric gels

Fig 5.1 shows the ^{27}Al MAS NMR spectrum of an alumina rich xerogel. This material was prepared using aluminium *isopropoxide*, tetraethyl silicate and butan-1-ol. The base solution was made up in the standard manner, stirred and then allowed to settle. The solution was allowed to separate into two layers, the lower layer appeared to contain a white suspension, the upper layer was relatively clear and colourless. The upper layer was removed and the remaining material was dried using the flowing hot air method. After drying and removal of the organics the material was examined by NMR. The aluminium in the system is seen to occupy predominantly octahedral environments, with relatively little tetrahedrally coordinated aluminium present.

Heat treatment of this material at 1300°C for 18 hours gave mainly alumina. This indicates that the upper layer was TEOS rich, the lower layer was rich in unreacted, or only partially reacted, aluminium *isopropoxide*. The solid aluminium alkoxide had simply settled out. The stoichiometry of the resultant material was not determined.

5.2.3 Stoichiometric gels

Figs 5.2 & 5.3 show the ^{27}Al MAS NMR spectra of various xerogels of mullite stoichiometry, all of which had been shown to be amorphous to x-rays. There is a significant variation in the shapes of these spectra although several common features exist. Within these gels, aluminium occupies sites of tetrahedral, Al(4), pentahedral, Al(5), and octahedral, Al(6), coordination. The variation between the gels is not in the sites occupied but in the relative intensities of the resonances, and hence the number of atoms in each type of environment. The difference between the gels themselves is only in the method of fabrication, so it can be readily seen that the method of fabrication affects the preferred aluminium environment.

The structure of these materials, as far as aluminium is concerned, is affected quite dramatically by the exact method of fabrication. Fig. 5.2 shows the spectra obtained from the xerogels GNW and GYW which were prepared from the same base solution. After 20 days stirring, the solution was split into two portions and to one portion, GYW, water was added. The synthesis method is given in more detail in chapter 4. The spectrum of the

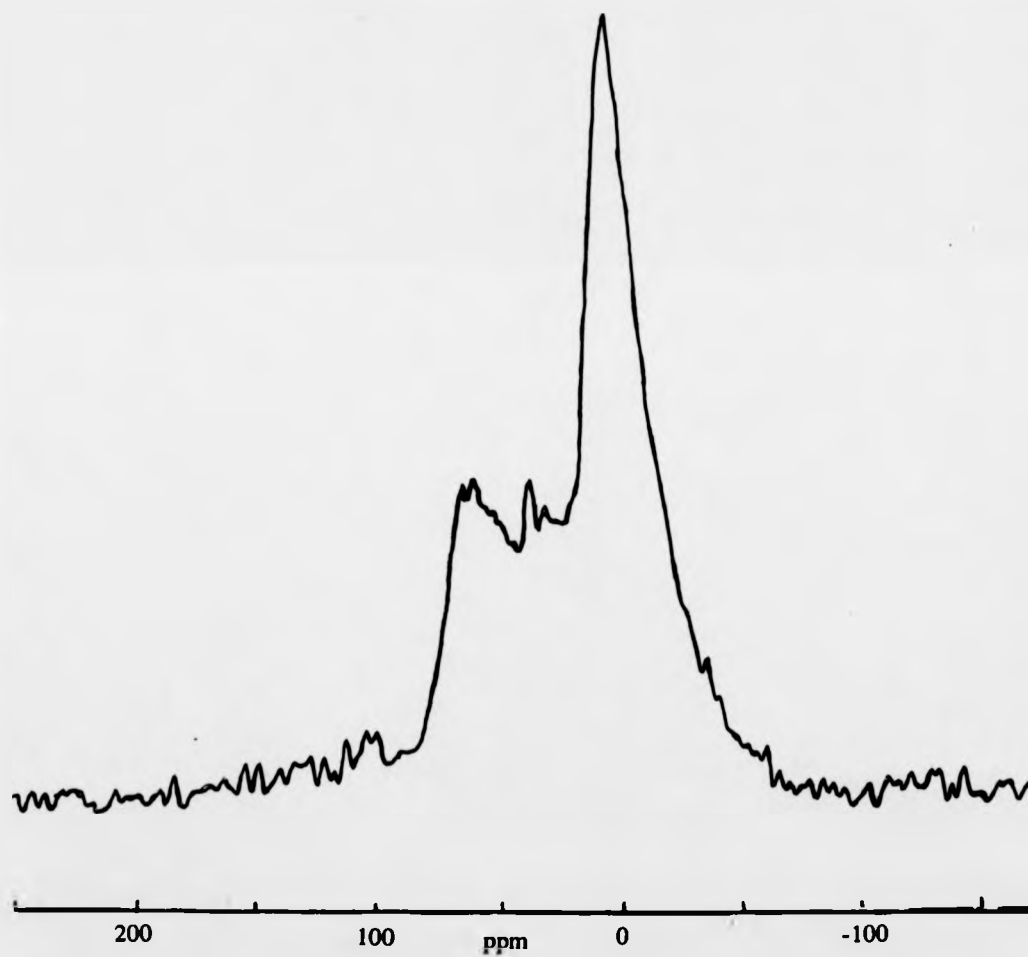


Figure 5.1) The ^{27}Al MAS NMR spectrum of an alumina rich xerogel.

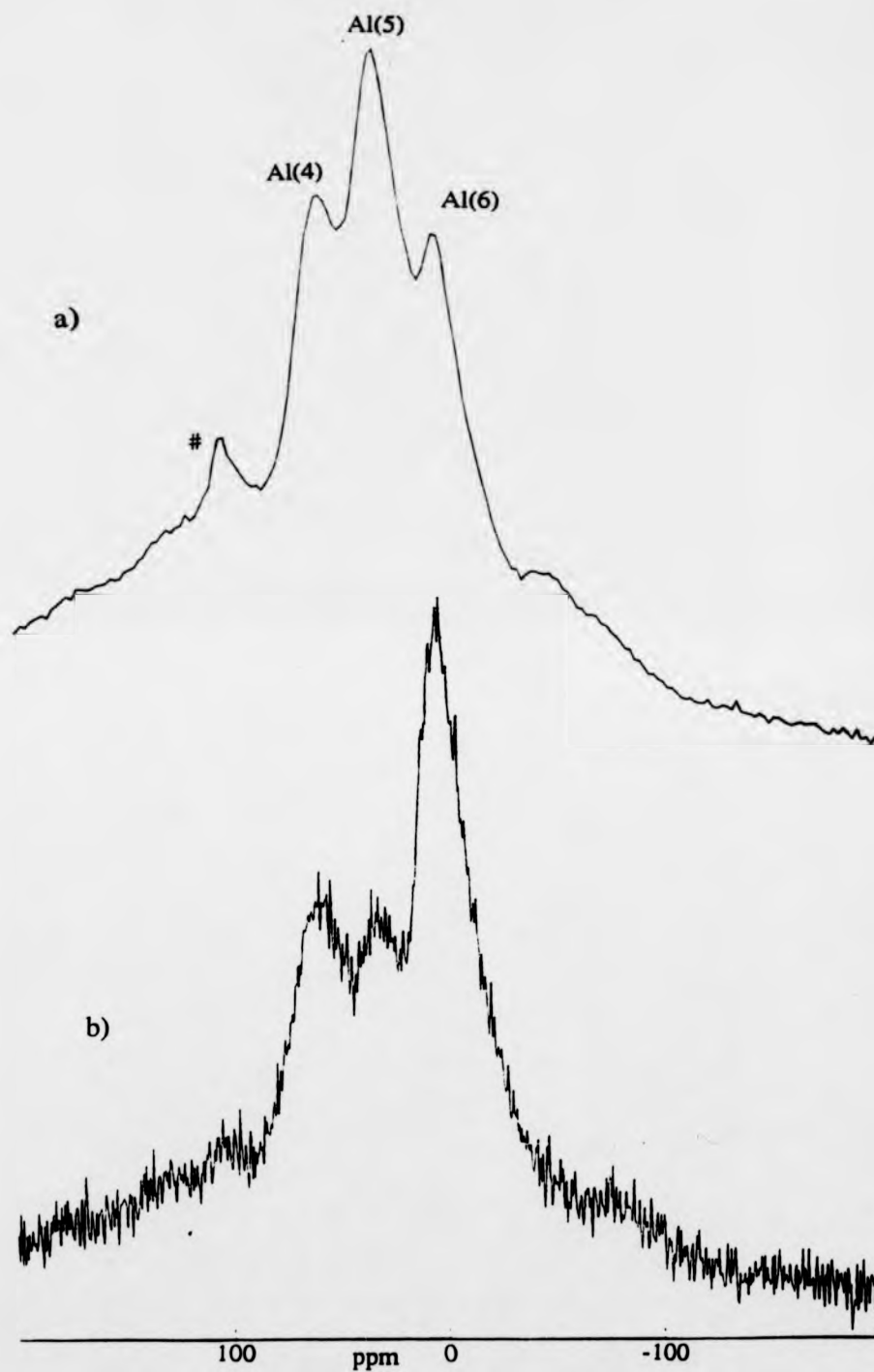


Figure 5.2) The ^{27}Al MAS NMR spectra of the xerogels of the materials a) GNW and b) GYW.

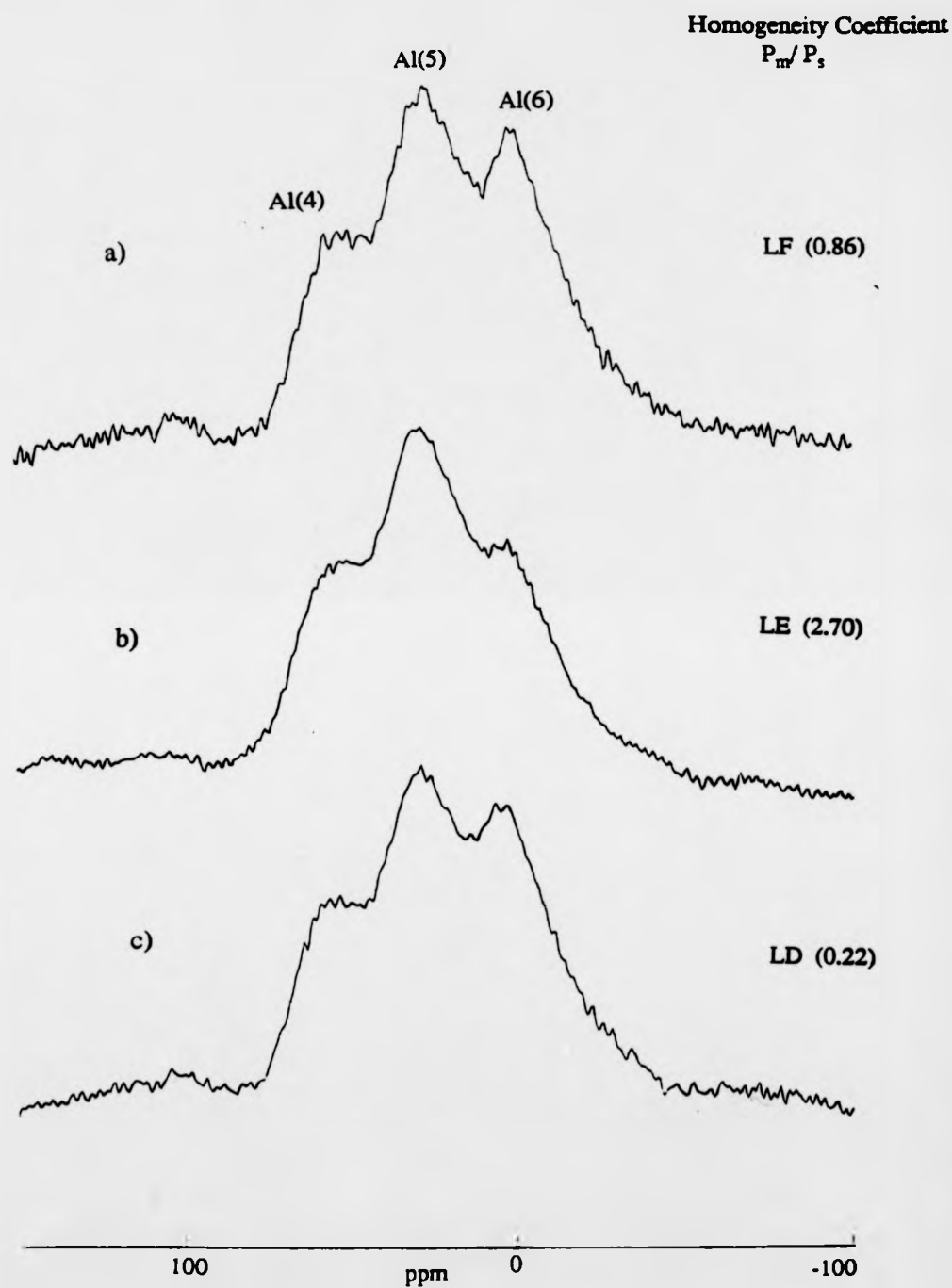


Figure 5.3) The ^{27}Al MAS NMR spectra of the xerogels a) LF, b) LE and c) LD.

material GNW shows aluminium preferentially occupying pentahedral and tetrahedral sites with octahedral coordination as a minority occupied environment, whereas in the material GYW octahedral aluminium is the preferred environment. The effect of the addition of water to the parent solution thus had a considerable effect on the structure that results after the heat treatment programme to yield the xerogel. The addition of water to the parent solution appears to favour the formation of octahedrally coordinated aluminium in comparison with the other two possible environments. The spectrum of the xerogel of GYW resembles that of the alumina rich compositions.

Figs 5.3 shows the spectra of three xerogels of the L-series. These spectra show features that are common with the gels already discussed, that is there are three aluminium environments, Al(4), Al(5) and Al(6). The only difference between the fabrication of these gels, is the length of time the base solution was stirred. It can be seen that, in relative terms, the xerogel of LE has significantly more pentahedral aluminium, LD has the most Al(6) and the structure of LF lies in between these two.

5.3 Post exotherm structure

5.3.1 X-ray diffraction

On completion of the 980°C exotherm the xerogels were analysed by XRD in order to determine the phases that had been formed and the relative amount of any mullite and spinel phase according to the semi-quantitative homogeneity coefficient defined in section 4.2.4.1.

The XRD patterns of the materials GYW and GNW after completion of the exotherm are shown in fig 5.4. GYW is seen to be mainly x-ray amorphous except for two peaks at d-spacings of ~ 2.0 and $\sim 1.4\text{\AA}$. These peaks are due to the presence of the spinel phase and no other crystalline phase is inferred from this pattern. The diffraction pattern of the sample GNW is significantly different, there appears to be only a small amount of any amorphous phase present and all the peaks that are observed correspond to mullite. Since no line splitting of the diffraction maxima from the (120)/(210) planes etc is seen, the equivalence of the *a* and *b* lattice parameters may be inferred, suggesting pseudotetragonal mullite.

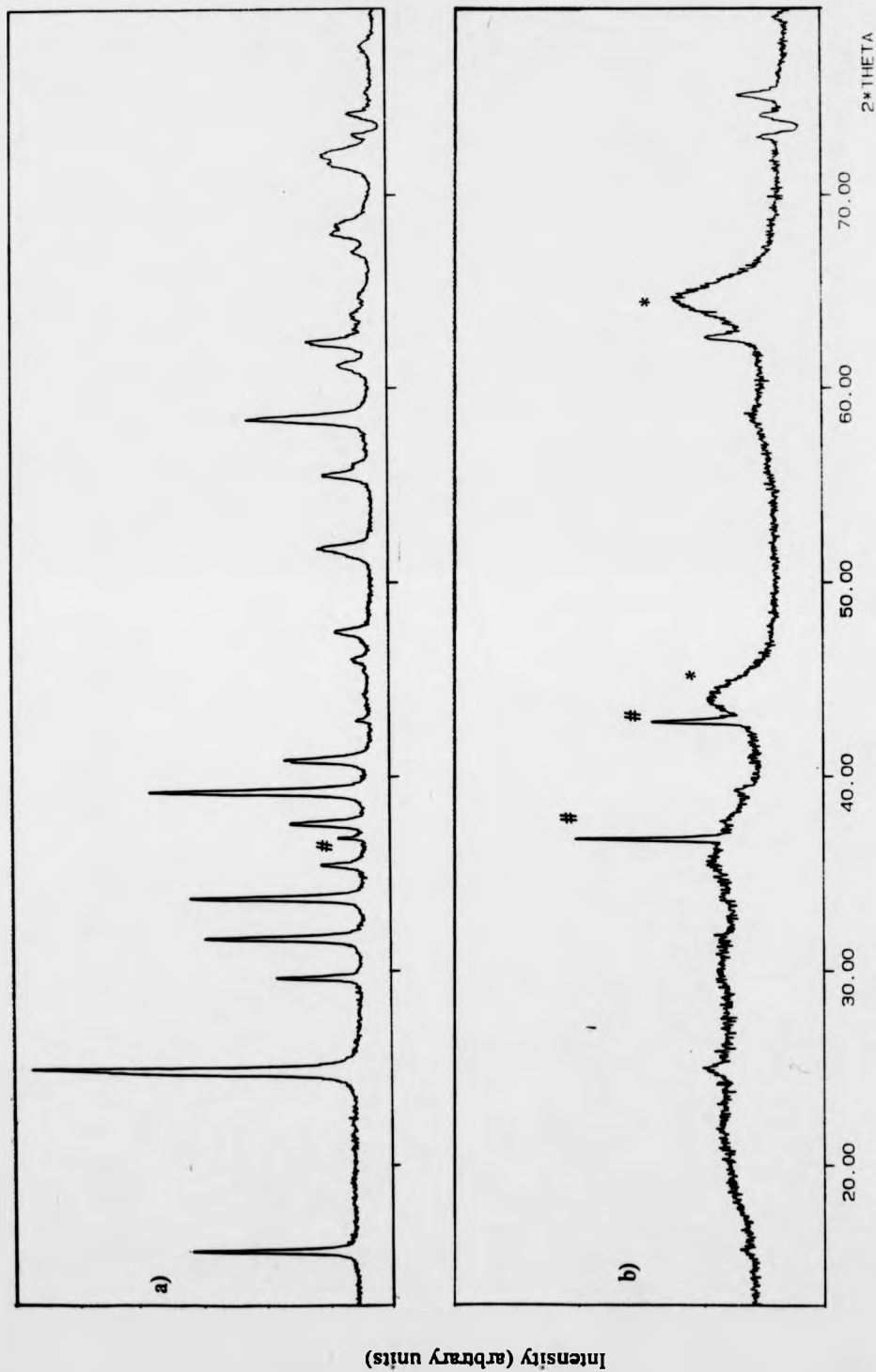


Figure 5.4) The X-ray diffraction patterns of the materials a) GNW and

b) GYW after completion of the 980°C exotherm.

* - spinel, # - aluminium holder, other peaks are due to mullite

The diffraction patterns of the materials LF, LE and LD after heat treatment to the completion of the exotherm are shown in fig 5.5. These materials contain a mixture pseudotetragonal mullite, spinel and an amorphous phase. These materials were characterised from these diffraction patterns, the values of their homogeneity coefficients were, LD = 0.22, LF = 0.86 and LE = 2.70. This relates to the low temperature structure in the same way as the trend seen with the gels GNW and GYW. That is, the sample with the most octahedrally coordinated aluminium, LD, had the lowest yield of mullite after 980°C, whilst the sample with the most pentahedral aluminium crystallised at this temperature to give the most mullite.

5.3.2 Nuclear Magnetic Resonance

Fig 5.6 shows the ^{27}Al MAS NMR spectrum of an orthorhombic mullite sample. The aluminium occupies two environments, octahedral and tetrahedral. There are two resonances for tetrahedral aluminium one at 42ppm the other at 60ppm.

Fig 5.7 shows the spectra of the samples GNW and GYW after heating to completion of the 980°C exotherm. The spectrum of GNW closely resembles that of the orthorhombic mullite material. GYW shows a significant difference in the distribution of aluminium over the two environments.

5.4 Low temperature heat treatments

5.4.1 X-ray diffraction

Four L-series materials were characterised in terms of their homogeneity by heating to completion of the exotherm, they had the following homogeneity coefficients;

$$\text{LC} = 0.32 \quad \text{LF} = 0.86 \quad \text{LG} = 1.66 \quad \text{LH} = 2.44$$

The amorphous xerogels of these materials were isothermally heated at 850°C for 100 hours and the x-ray diffraction patterns of the resultant materials are presented in fig.5.8. The material that had been characterised as the least homogeneous (LC) had partly devitrified to the spinel phase and some mullite. The gel considered as the most homogeneous (LH), did not appear to have undergone any devitrification after this treatment. The other two gels, of intermediate homogeneity partially devitrified to mullite

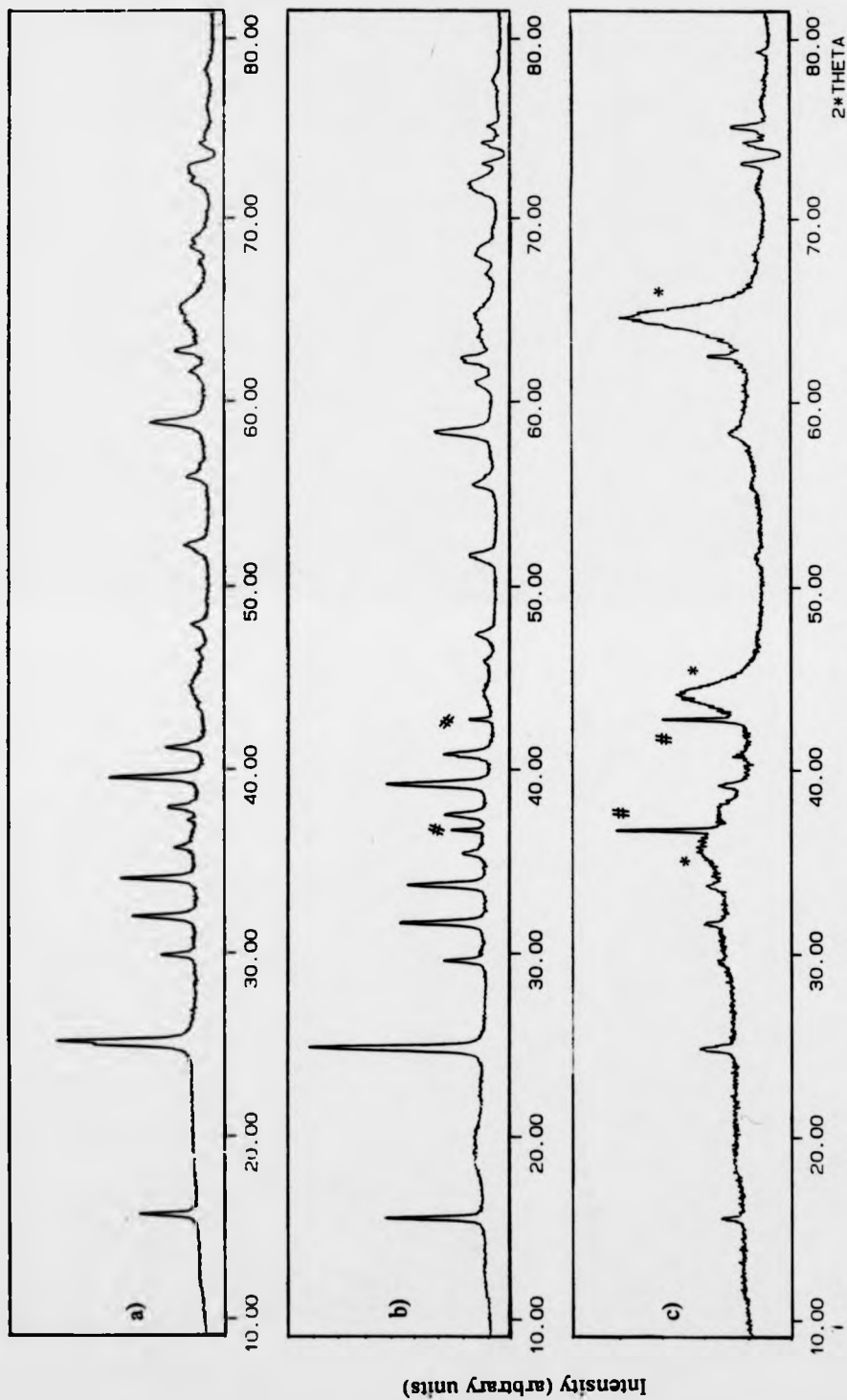


Figure 5.5) The X-ray diffraction patterns of the materials a) LF, b) LE

& c) LD after completion of the 980°C exotherm.

* - spinel, # - aluminium holder, other peaks are due to mullite

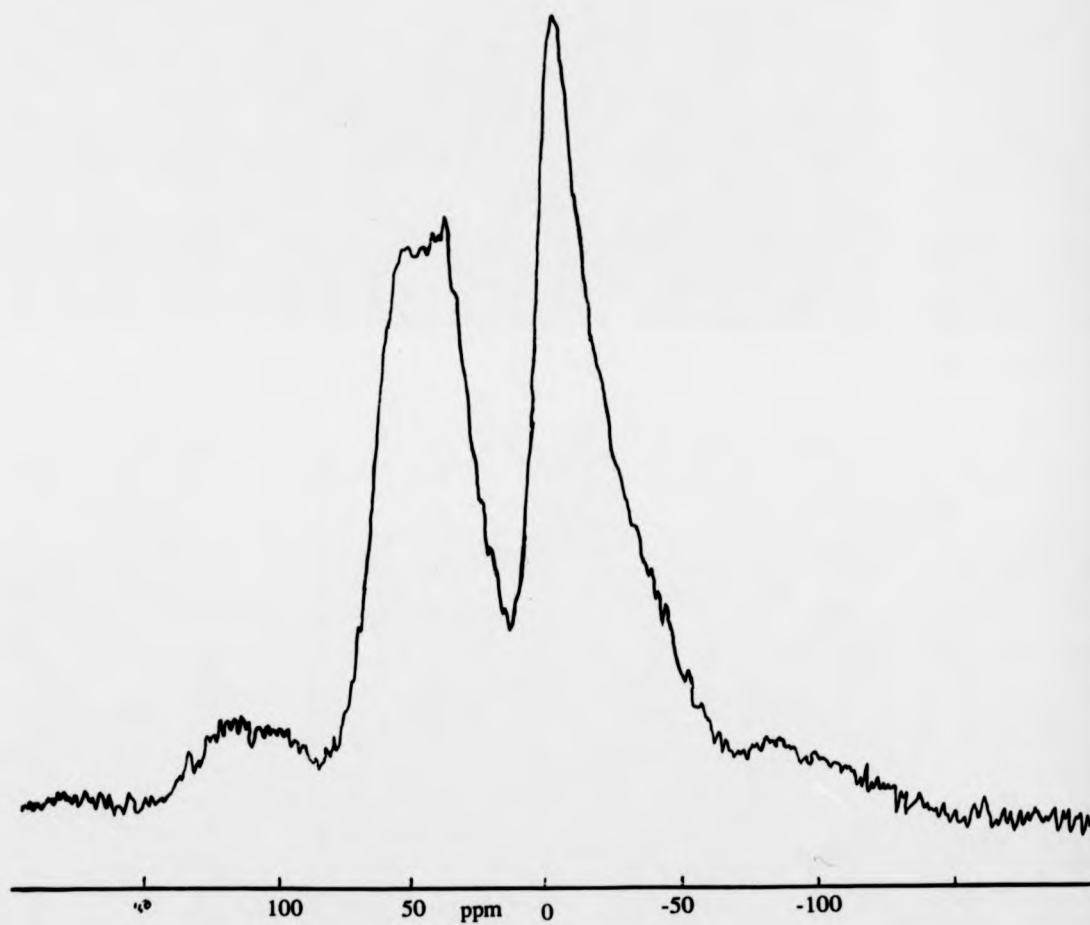


Figure 5.6) The ^{27}Al MAS NMR spectrum of orthorhombic mullite.

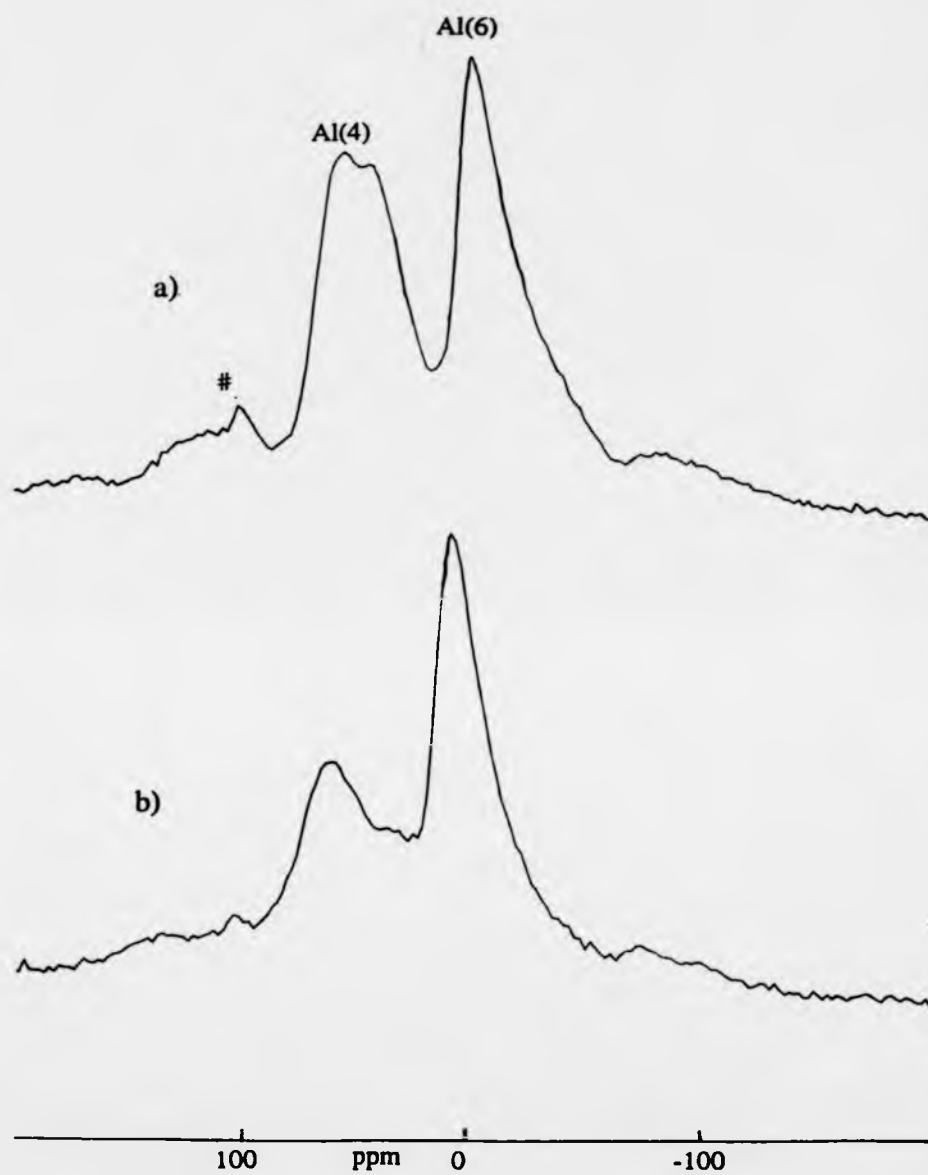


Figure 5.7) The ^{27}Al MAS NMR spectra of the materials a) GNW and
b) GYW after completion of the 980°C exotherm.

- AlN in rotor

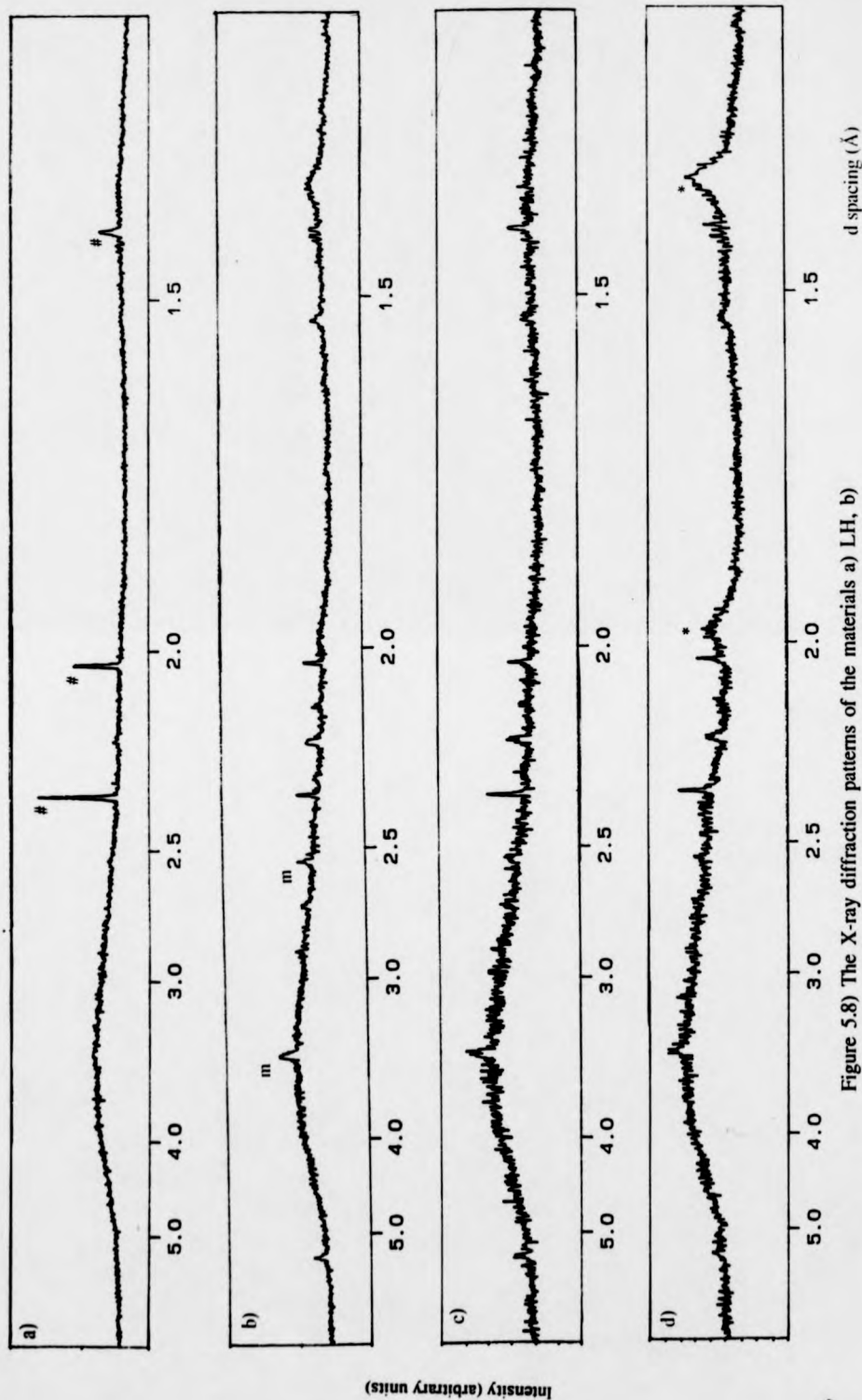


Figure 5.8) The X-ray diffraction patterns of the materials a) LH, b)

LG, c) LF and LC after heat treating the alcogels at 850°C

for 100 hours.

* - spinel, # - aluminium holder, other peaks are due to mullite

and spinel.

On the amorphous xerogels of materials of the same preparations a higher temperature isothermal heating programme was carried out. The xerogels were held at 940°C for 10 hours. Fig 5.9 shows the diffraction patterns of the materials after this heat treatment. The behaviour of the gels was considerably different after this higher temperature isothermal soaking. The least homogenous contained a significant amount of spinel, the most homogeneous correspondingly devitrified to essentially mullite alone. Fig 5.10 shows an expanded view of the diffraction peak at about 3.4Å from the sample LH. This peak is due to reflections from planes parallel to the *c* axis and with $(h^2 + k^2) = 5$. This peak clearly shows evidence of line splitting, that is there are reflections from planes (120) and (210) where the *a* and *b* lattice parameters are not equal. This sample thus contains, as evidenced by the incomplete peak splitting, pseudotetragonal and orthorhombic mullite. LF and LG showed behaviour that was not consistent with the general trend. LG, nominally the more homogeneous had partially crystallised to mainly spinel whilst LF had mullite as the predominant crystalline phase.

5.4.2 NMR

Fig 5.11 shows the ^{27}Al MAS NMR spectra of the gel LH after both the sub-exotherm heat treatments. After 100 hours at 850°C aluminium is found in 4-, 5- and 6-fold coordination. The amount of pentacoordinate aluminium present is quite significant. After only 10 hours at 940°C the structure of the material is very different, the aluminium resides only in sites of tetrahedral and octahedral coordination. The higher temperature heat treatment appeared to have removed all of the pentacoordinated aluminium.

5.4.3 Thermal analysis

As a comparison an amorphous xerogel of sample LH was heated under the usual conditions in thermal analysis equipment to the completion of the exotherm. The sample that had been isothermally soaked at 940°C for 10 hours was then subjected to an identical thermal analysis schedule. Fig 5.12 shows the resultant DTA traces. The isothermally treated sample, which had had all the pentacoordinated aluminium removed, showed no

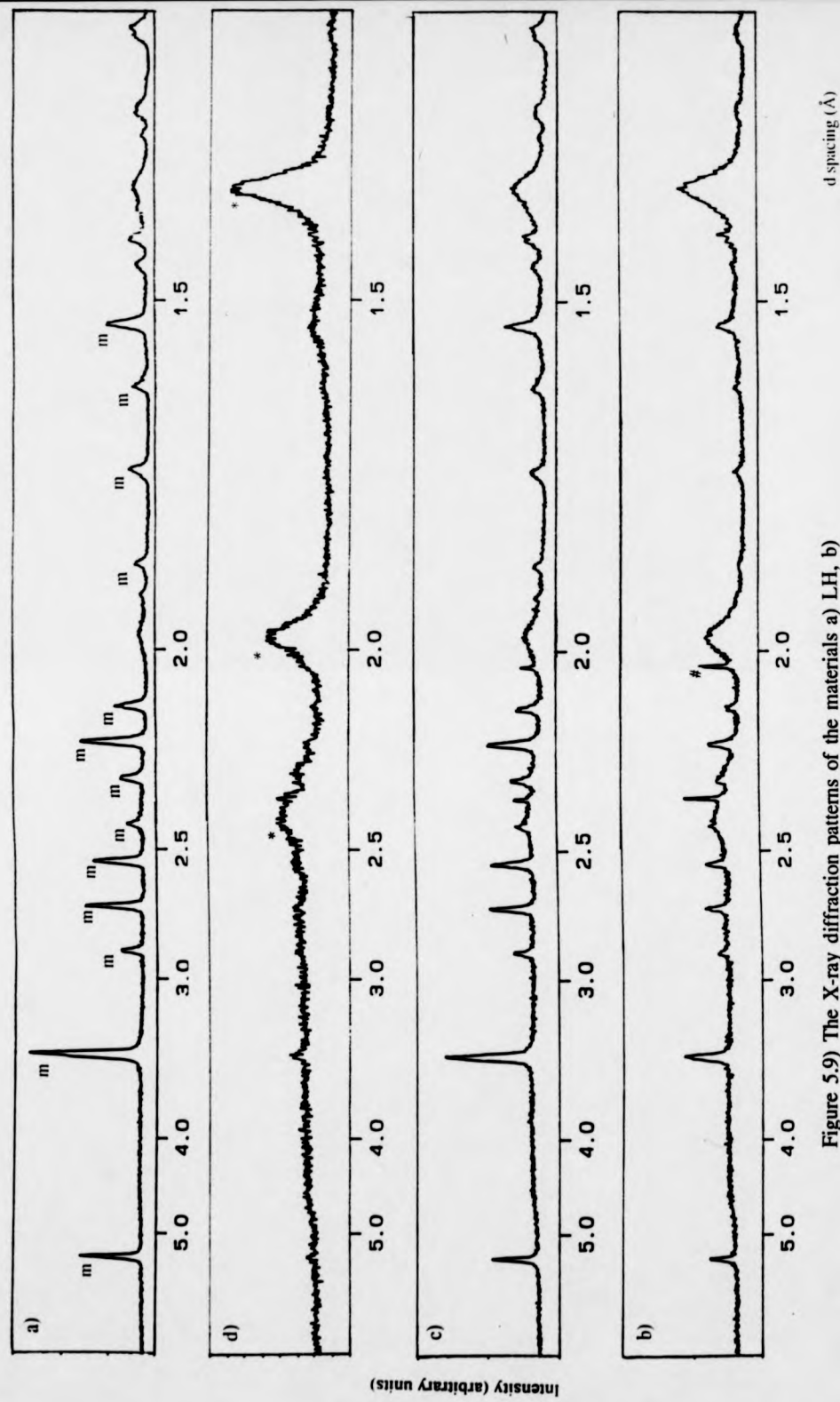


Figure 5.9) The X-ray diffraction patterns of the materials a) LH, b)

LG, c) LF and LC after heat treating the alcogels at 940°C

for 10 hours.

* - spinel, # - aluminium holder, other peaks are due to mullite

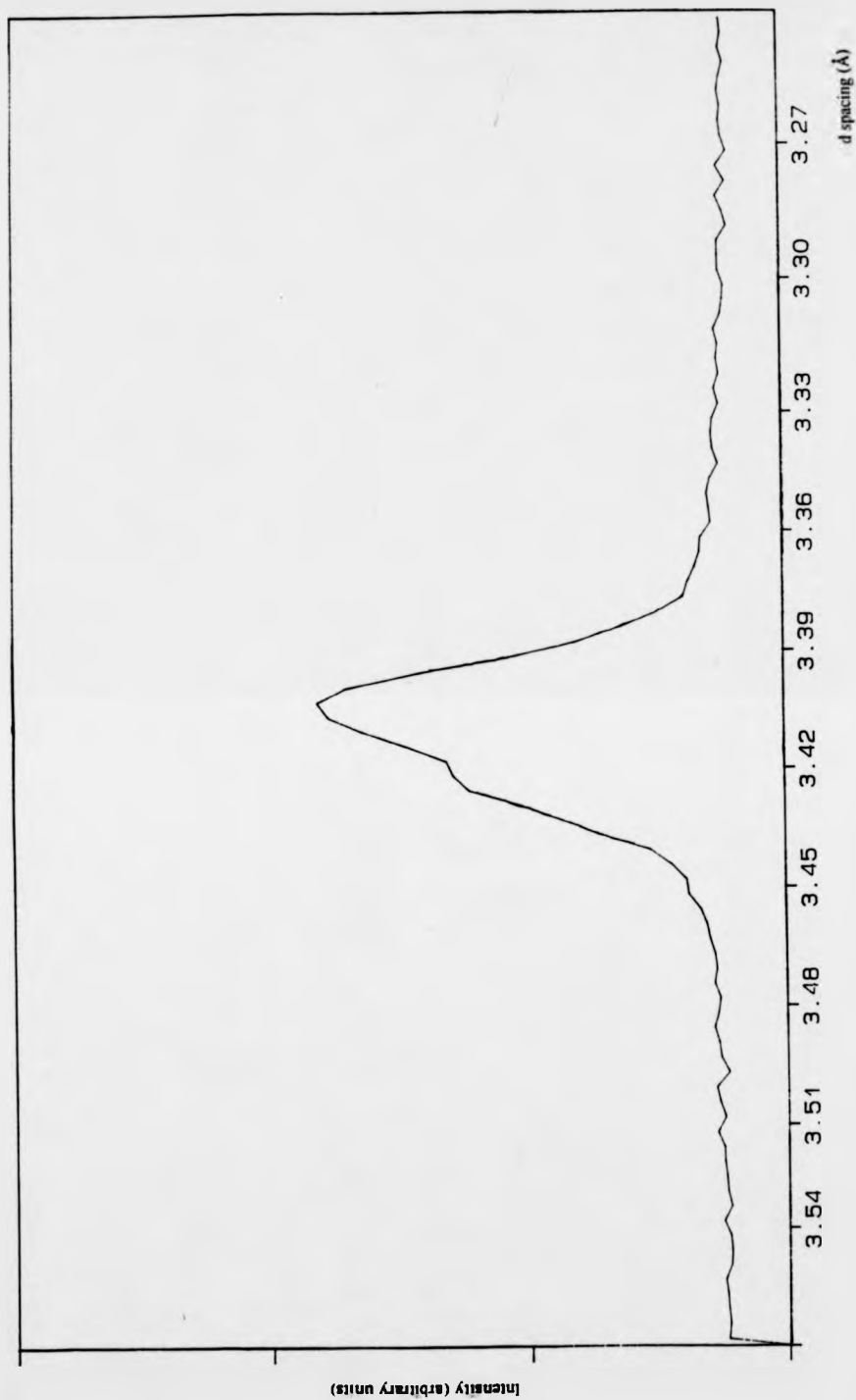


Figure 5.10) An expanded view of the peak occurring at approximately

3.4Å in the X-ray diffraction pattern of the material LH

after it had been heated at 940°C for 10 hours.

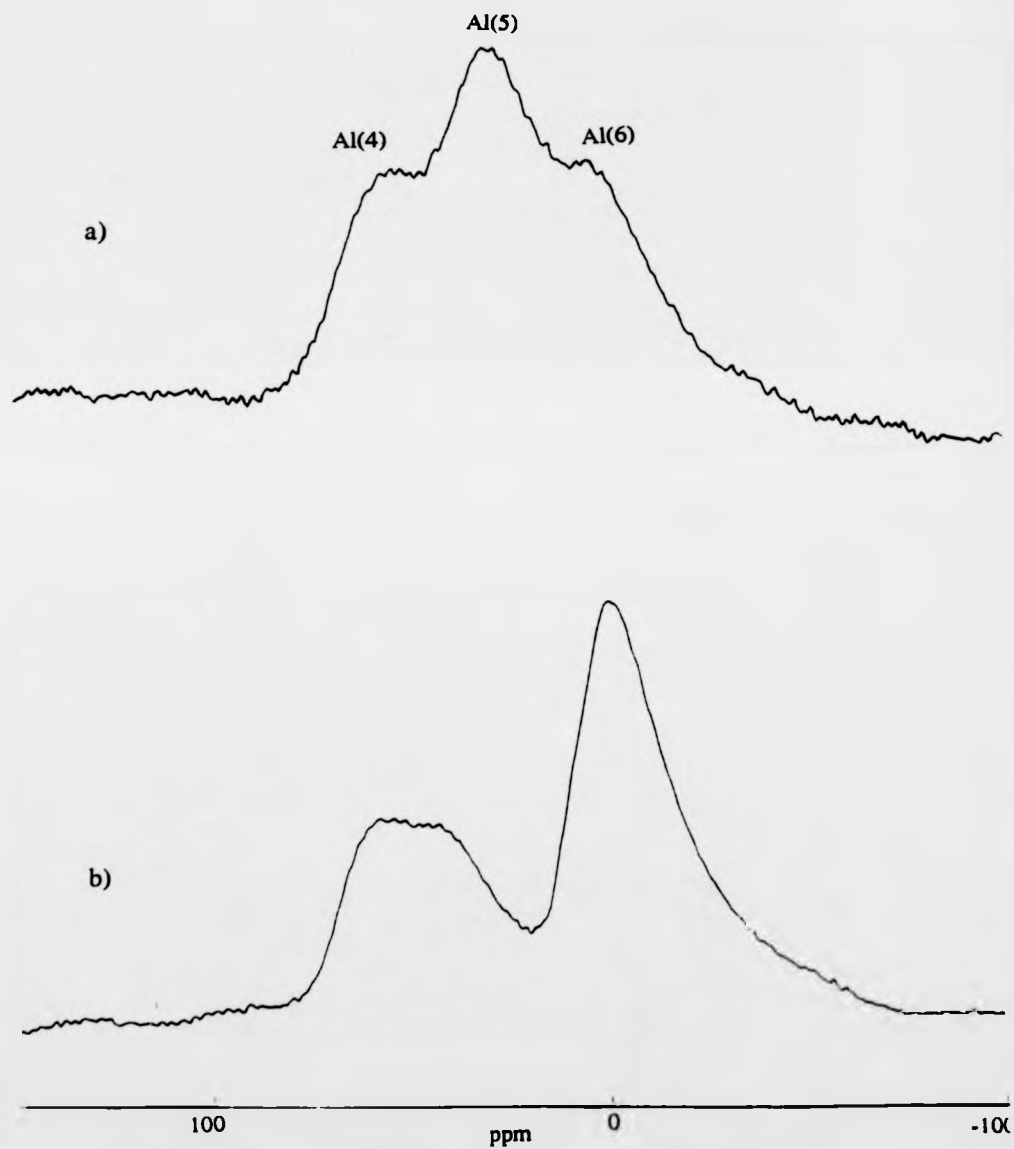


Figure 5.11) The ^{27}Al MAS NMR spectra of the material LH after the alcogel had been heated a) at 850°C for 100 hours and b) 940°C for 10 hours.

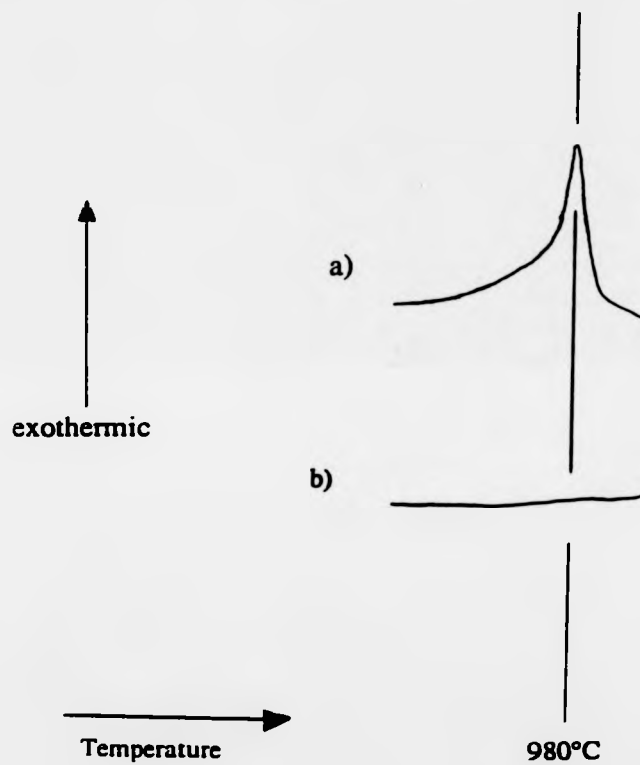


Figure 5.12) The differential thermal behaviour at approximately 980°C of a) the xerogel of the material LH and b) the alcogel after it had been heat treated at 940°C for 10 hours.

exotherm at 980°C, indeed this sample showed no thermal behaviour at all over the temperature range used, 20°C - 1000°C.

5.4.4 X-ray diffraction of sample LH

The x-ray diffraction pattern of LH after the low temperature heat treatment of 10 hours at 940°C is shown in fig. 5.9 (d). When this material had subsequently been heated to 995°C (the usual temperature for homogeneity characterisation) in thermal analysis equipment it was analysed by X-ray diffraction. The resultant pattern is shown in fig. 5.13, it can be seen comparing these two patterns that no significant difference exists. The heating of this material to a temperature where the exotherm should occur, thus has no effect on the relative amounts of spinel and mullite, probably also on the total degree of crystallinity of the material.

5.5 High temperature heat treatment

5.5.1 X-ray diffraction

Three samples of the amorphous xerogel of material LD were heat treated in thermal analysis equipment to the following temperatures, 1000°C, 1270°C and 1400°C. The XRD patterns of the resultant materials are shown in fig 5.14. After completion of the 980°C exotherm the dominant crystalline phase is spinel. Continued heating yields an increase in the amount of mullite though spinel remains the dominant crystalline phase. There appears to be some splitting of the (120) reflection indicating the presence of some orthorhombic mullite. The high temperature exotherm that is associated with this transformation was not observed. Further heating still, to 1400°C gave a material which was a mixture of orthorhombic mullite and corundum, the spinel phase was not observed after treatment to this high temperature. Again the high temperature exotherm associated with the transformation of orthorhombic from pseudotetragonal mullite was not observed. The exotherm that would be expected from the crystallisation of the corundum was also not observed under these conditions.

Fig 5.15 shows the analogous heat treatments carried out on a more homogeneous material, LB. After completion of the exotherm pseudotetragonal mullite was the major

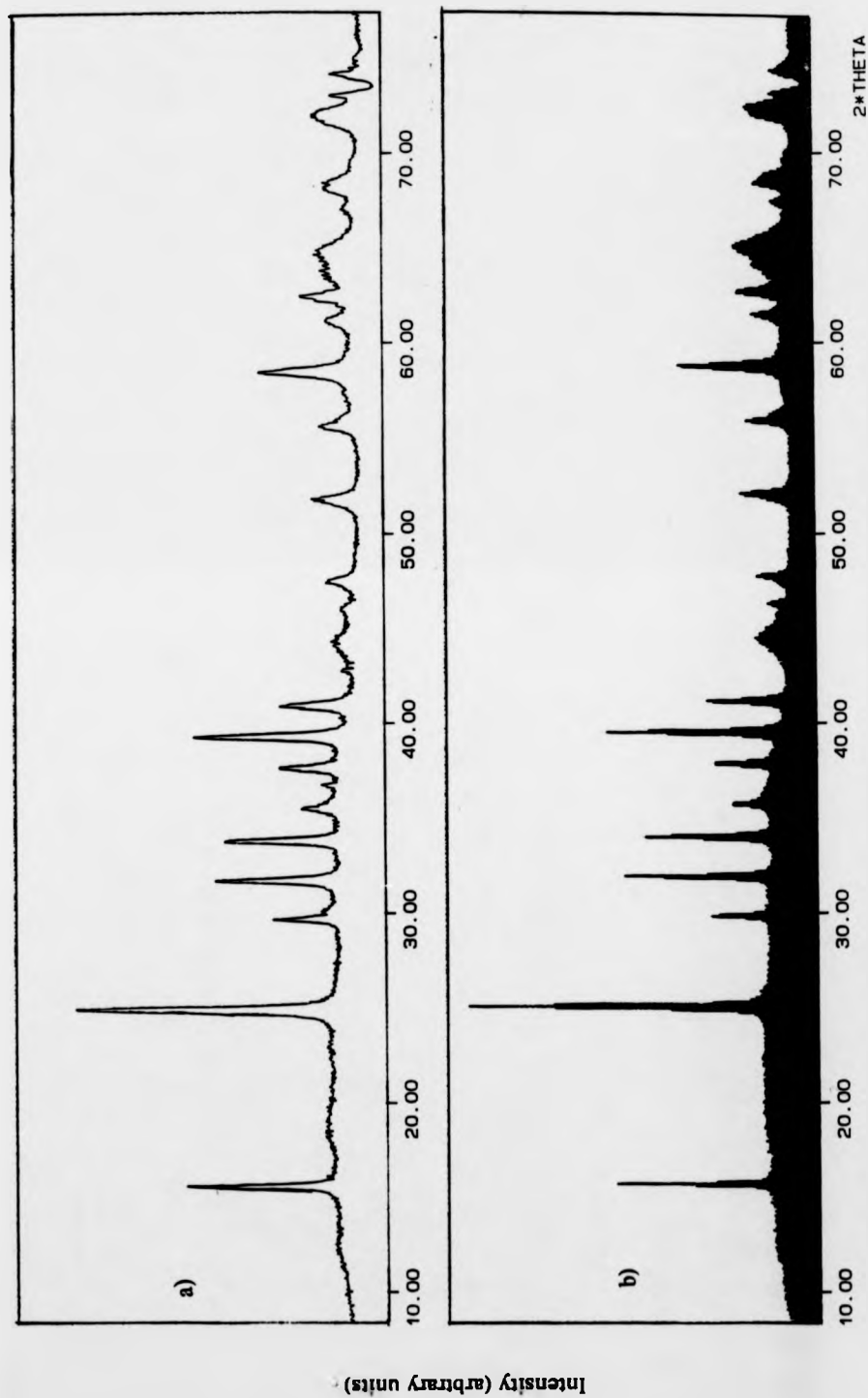


Figure 5.13) The X-ray diffraction pattern of a) the xerogel of LH after being heated to completion of the 980°C exotherm, and b) the 940°C (10 hours) sample of LH after being heated to approximately 1000°C in the DTA equipment.

* - peaks due to spinel, all other peaks are due to mullite.

NB: pattern b) is coloured in due to an instrumental effect.

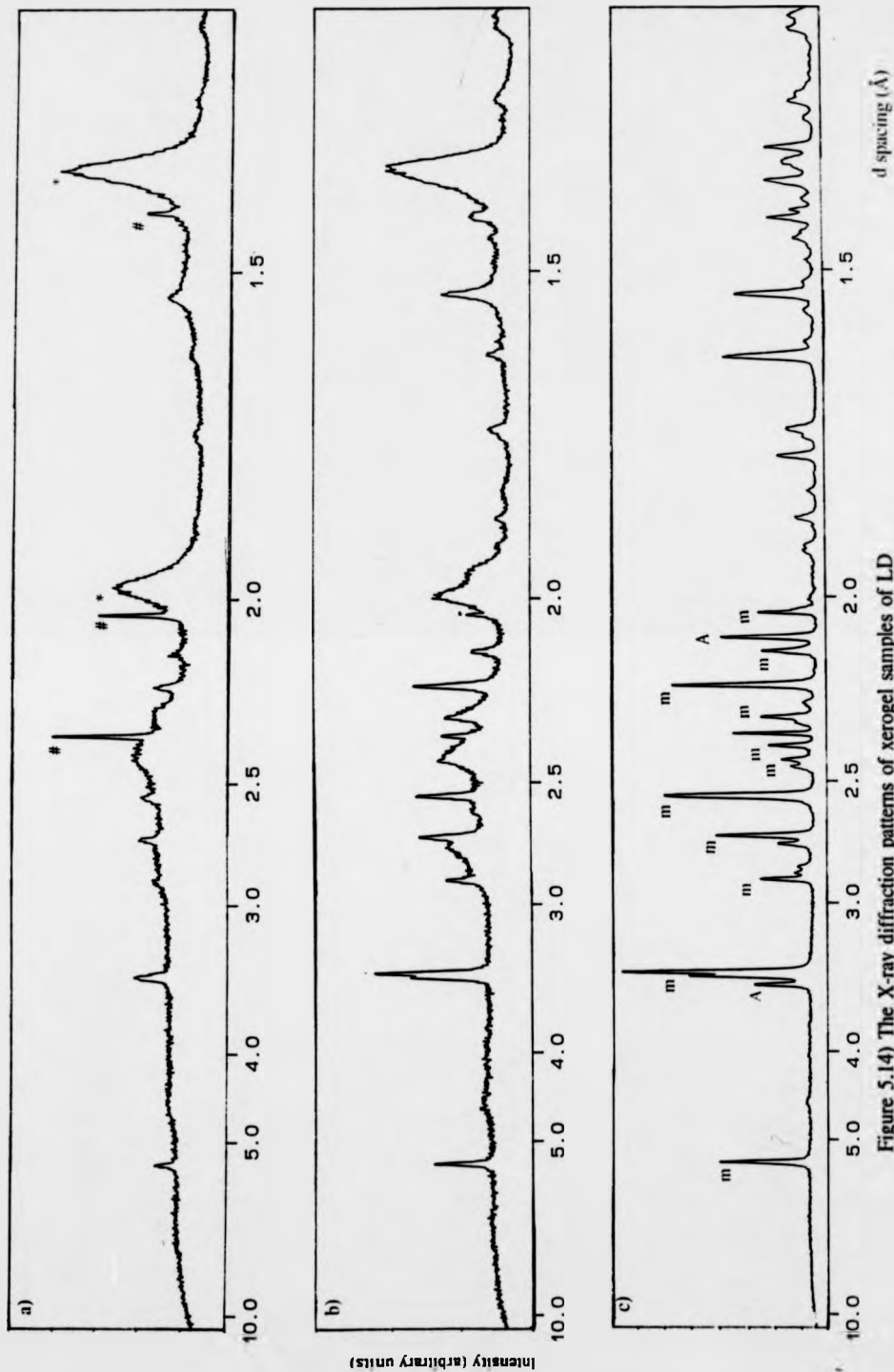


Figure 5.14) The X-ray diffraction patterns of xerogel samples of LD

after further heat treatments in DTA equipment to a) 1000°C, b) 1270°C and c) 1400°C.

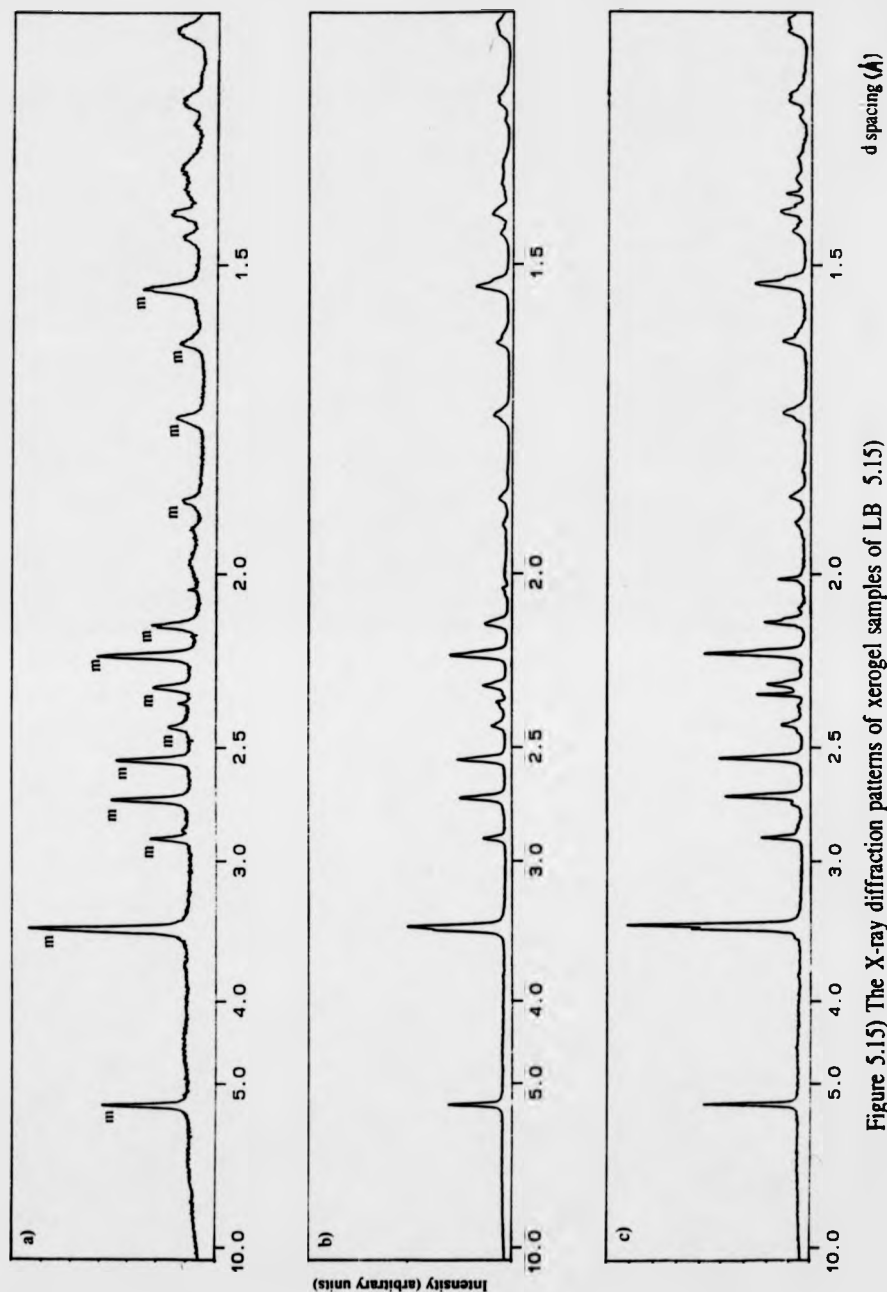


Figure 5.15) The X-ray diffraction patterns of xerogel samples of LB 5.15)

after further heat treatments in DTA equipment to a)

1000°C, b) 1270°C and c) 1400°C.

m - mullite

crystalline phase, a trace amount of spinel was observed. Continued heating to 1270°C gave a material where no spinel was readily observed. Some peak splitting of the (120) reflection indicates that some transformation to the orthorhombic form had taken place. The exotherm associated with this event was not observed on this heat treatment, or when the xerogel was heated to 1400°C. After heating to this higher temperature the only crystalline phase that could be detected was orthorhombic mullite.

The diffraction patterns obtained from samples LB and LD, after these heat treatments were used to calculate the lattice parameters of the observed mullite. These are presented in table 5.1. The patterns from the samples that had been heated to 1270°C were treated as tetragonal since the amount of peak splitting was insufficient to allow separate peak position measurements.

Using the graph of the a lattice parameter against composition as presented by Cameron [104], it can be readily seen that the tetragonal mullites are significantly richer in alumina than the orthorhombic mullites, fig 5.16.

Table 5.1
Lattice parameter estimation

After 1000°C in the DTA						
Sample	Phases Present		a_o (Å)	b_o (Å)	c_o (Å)	cell volume (Å ³)
After 1000°C in the DTA						
LB	M,S & A	T	7.62	7.62	2.878	167.3
LD	M,S & A	T	7.62	7.62	2.875	166.8
After 1270°C in the DTA						
LB	M,S & A	T	7.62	7.62	2.872	166.9
LD	M,S & A	T	7.63	7.63	2.877	167.5
After 1400°C in the DTA						
LB	M,S & A	O	7.57	7.61	2.872	165.5

Where M = mullite, S = spinel and A = amorphous. The lattices were considered to be either tetragonal (T) or orthorhombic (O), depending on whether the (120) and (210) line splitting was observed and allowed separate peak position measurement. The values quoted are precise to the nearest significant figure.

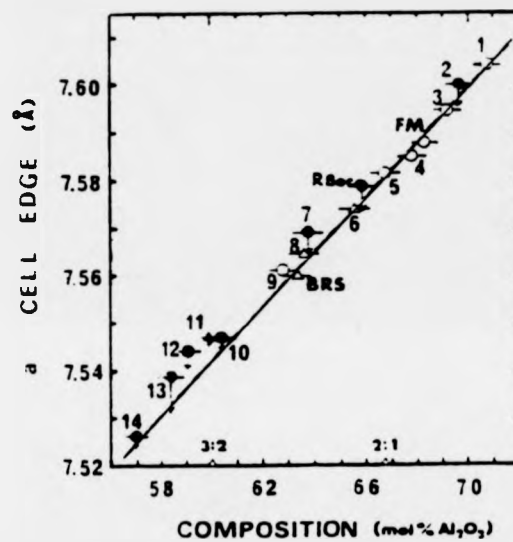


Figure 5.16) Variation in the alumina content of various mullites with lattice parameter a_0 (After Cameron [104])

5.6 Summary of results

Materials have been produced that undergo a degree of crystallisation on heating to 980°C. The phases that may be observed after such a heat treatment are mullite, a cubic spinel type phase or both these crystalline phases together. A residual amorphous phase is always seen. The structure of the amorphous xerogel appears to play a central role in determining the nature and the relative amounts of the crystalline phases that are yielded. The results obtained from ^{27}Al MAS NMR of the xerogels seem to indicate relationships between the most populated coordination sites of aluminum in the xerogel and the crystalline nature of the material after heating to the completion of the 980°C exotherm. When octahedral coordination is the preferred environment in the xerogel, spinel is the major crystalline phase after devitrification. When aluminium is preferentially pentacoordinated (with respect to the amount of octahedral coordinated aluminium) mullite is the preferred resultant crystalline phase.

Heating of an homogeneous xerogel to the completion of the exotherm yields a mullite that has a pseudotetragonal structure, and is alumina rich. The environments about aluminium for this material are similar to those in orthorhombic, stoichiometric mullite, the only difference possibly being in the relative amounts of the two types of tetragonally coordinated aluminium. Continued heating of the pseudotetragonal mullite causes it to transform to the orthorhombic form. This probably occurs as a reaction with the silica rich amorphous matrix.

Heating of an inhomogeneous material initially yields spinel as the major crystalline phase, further heating causes an increase in the amount of pseudotetragonal mullite. Continued heating causes the transformation of the pseudotetragonal mullite to the orthorhombic form. The formation of α -alumina (corundum) is also resultant on heating of an inhomogeneous material at a constant, rapid heating rate. This phase is likely to be due to the transformation of alumina rich regions of spinel to the stable high temperature form of alumina. A long time heat treatment at a temperature above that of the main exotherm, but below that needed for the formation of corundum, allows the full reaction of the amorphous silica rich matrix with the alumina rich crystalline phases giving orthorhombic mullite.

Isothermal heating of the xerogels, below the temperature of the exotherm, causes those gels that have been characterised as inhomogeneous to devitrify to mainly spinel. Aluminium in the cubic spinel phase is predominantly octahedrally coordinated. Thus the coordination of aluminium does not change on devitrification to the spinel phase, either below or above the exotherm temperature. Homogeneous gels, however, devitrify to mullite at sub-exotherm temperatures.

Pentacoordinated aluminium is observed in samples that have not been heated above 980°C, or in samples that have not been isothermally soaked below this temperature for a long time. When a material has been caused to partially crystallise below the exotherm

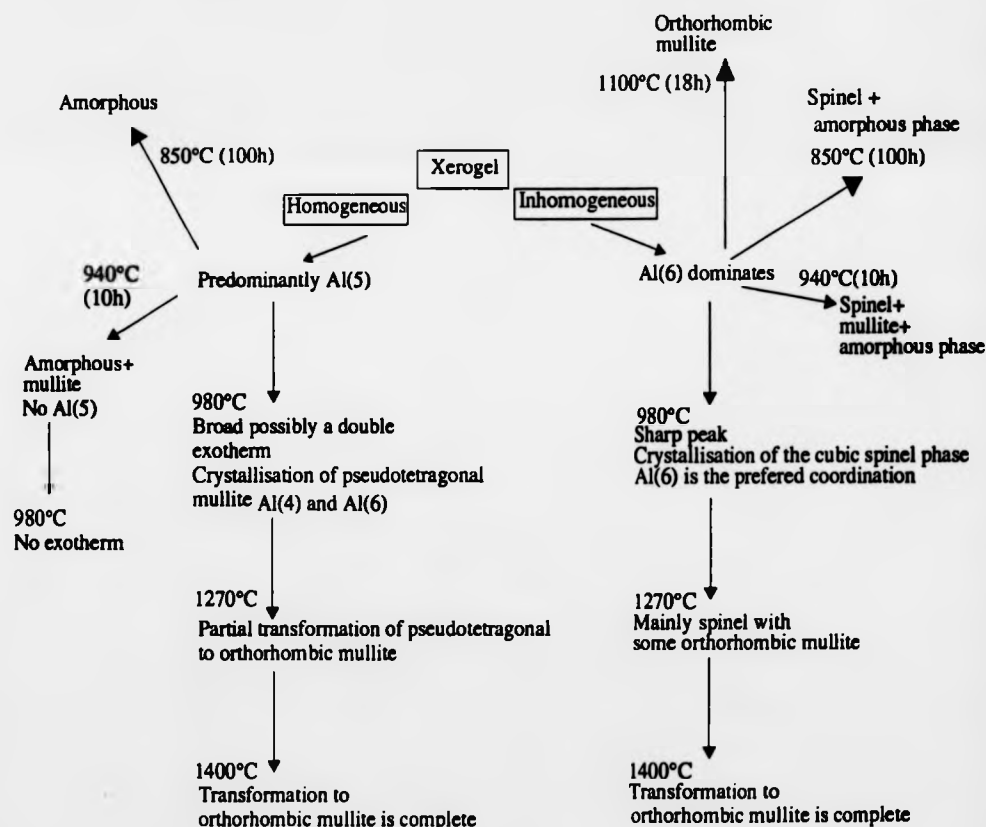


Figure 5.17 A schematic summary of the crystallisation behaviour of homogenous and inhomogeneous xerogels of mullite stoichiometry.

temperature, and the pentacoordinate aluminium is removed during this process, the material no longer exhibits the exotherm on heating to the relevant temperature.

A summary of the crystallisation behaviour of homogeneous and inhomogeneous xerogels is shown above in fig. 5.17.

5.7 Discussion

Octahedral aluminium in the xerogel appears to be indicative of inhomogeneity. The crystalline forms of alumina favour octahedral aluminium, this corresponds well with the structure of materials containing spinel as the major crystalline phase. This may suggest that alumina may be present as discrete inhomogeneities within the amorphous matrix of the gel. The formation of such alumina rich regions in the fabrication of aluminosilicates by sol-gel techniques has been previously discussed in chapter 1. If such regions do exist then they are likely to influence strongly the detailed crystallisation processes.

As the volume of individual inhomogeneities decreases, that is as the bulk material becomes more homogeneous, the interfacial area between the inhomogeneities and the matrix correspondingly grows. Considering the stoichiometry of mullite there must be clusters of alumina polyhedra, even when the coordination polyhedra of alumina and silica are at the maximum degree of mixing. The interfacial region plays an important role in determining the character of the ceramic after heating to the completion of the exotherm. At low degrees of mixing, where the clusters are relatively large, this interface is where the rearrangement of alumina and silica takes place to yield a small amount of mullite. This is the situation described by the coprecipitated gel model of Okada and Ôtsuka [82]. The interface is also the boundary within which spinel is formed, inside the alumina rich region. It appears that there may be a link between the increase in the homogeneity, as indicated by the amount of Al(4) and Al(5), particularly Al(5) and the interfacial surface area between the inhomogeneities and the matrix. The pentacoordinated aluminium may exist at the interface of the inhomogeneities and the matrix. Tetrahedral coordination is the environment in which aluminium resides in a glassy network, octahedral coordination is the aluminum environment in very alumina rich regions (x-ray amorphous or crystalline). Pentacoordinate aluminium may exist at the interface of these two types of environment,

being stabilised by the interfacial strain between the two, or possibly minimising this strain. Alternatively this form of aluminium may be stabilised by the presence of silica polyhedra in close proximity to it.

Heat treatments of the materials produced may be split into two broad categories, isothermal soaking and rapid heating. The rapid, thermal analysis type heating nearly always produced an exothermic event at 980°C, below this temperature the xerogels were amorphous. The 980°C exotherm is associated with a crystallisation, the phases yielded by this crystallisation were mullite and spinel, the proportion of these phases depending on the homogeneity of the sample. The sub-exotherm isothermal soaking of these material causes their devitrification, the phases that crystallise out are in general agreement with the homogeneity of the materials as measured by the thermal analysis heating / X-ray diffraction technique. That is, materials defined as inhomogeneous also crystallise mainly to spinel, on sub-exotherm isothermal soaking. Homogeneous materials appear to be more stable to low temperature heating, when they crystallise it is mainly to mullite.

When the pentacoordinated aluminium is removed by sub-980°C heat treatments the exotherm is no longer observed. This may be due to the fact that the material has been crystallised and therefore no more transformation takes place, or it may be due to the fact that the pentacoordinated aluminium is missing from the sample.

The results obtained indicate that this polyhedron is intimately linked to the exotherm in two ways. On one level the polyhedron is metastable and at 980°C disproportionates to Al(4) and Al(6), and at the same time the amount of the polyhedron in the material influences the relative amounts of the two crystalline phases produced. This metastable arrangement of aluminium and oxygen undergoes a rapid displacive transformation at 980°C. The local silica and alumina polyhedra are also involved in this rearrangement and at the interface the mullite is produced because of the proximity of the two. Because the primary cause of this crystallisation is the rearrangement of a type of alumina polyhedra, more alumina than silica is necessarily involved and hence the form of mullite that is formed is the alumina rich 2/1 pseudotetragonal mullite. The alumina rich interior of the inhomogeneities is x-ray amorphous prior to 980°C. At this temperature the energy liberated by the transformation of Al(5) provides the activation energy for the alumina

which is primarily octahedral, to crystallise to spinel.

The low temperature devitrification of these materials to either spinel and/or mullite can be explained by the destabilisation of the metastable pentacoordinate polyhedra and the reorganisation of the inhomogeneities.

Considering the kaolin sample studied by Sanz [111] a significant amount of pentacoordinated aluminium was observed. The primary phase on crystallisation was spinel however. Kaolin has a layer structure and so layers of alumina and silica in contact exist. This gives intimate mixing of the polyhedra in the plane normal to the layers, but essentially zero mixing within the plane of the layers. Hence pentacoordinated alumina could exist and would be stabilised by the silica in the neighbouring layers. On heating, the metastable alumina polyhedra dissociate at 980°C, the structure of the kaolin is wrong for the formation of mullite. Spinel will be thus be produced as this is energetically favourable to the diffusion of silicon to give mullite.

Chapter 6

Discussion and conclusions

6.1 General Discussion

The original aims of this project were to devise a synthesis route for the fabrication of very dense mullite at relatively low temperatures. The materials characteristics of the mullite produced could then be established, with the general aim of identifying the most suitable point within the fabrication procedure where the incorporation of reinforcement agents could be carried out.

A particular pathway was chosen to give the information required by this aim. The obvious, and most important, consideration was to establish a method to produce mullite by sol-gel methods.

Sol-gel methods to yield mullite have been established by many researchers (see chapters 1 & 2). The routes used have been based on colloidal and alkoxide sol-gel, the pyrolysis of the alkoxides has also been carried out. The yield of mullite that is produced by the colloidal and alkoxide routes that have been tried ranges from very little to a significant amount. The initial direction of this study was to maximise the amount of mullite yielded at 980°C. This invariant temperature is well known and well documented in this small branch of materials science, it is also a very important temperature in the study of kaolin minerals. Any method to synthesise a material with a significant amount of aluminium and silicon must take account of this temperature and, more specifically the things that occur at 980°C. The work done in this field by other workers can be broadly split into two segments, low and high mullite yield at 980°C. High mullite yield means a material that is highly crystalline after heat treatment at this temperature, this leads to the difficulties in densifying the material. Low mullite yield indicates a low degree of mixing of the aluminium and silicon coordination polyhedra, the major crystalline phase produced at 980°C is the spinel phase. The segregation of alumina and silica in these materials may allow a significant amount of densification due to the viscous flow of the free silica, further heat treatment will not allow the crystallisation of mullite until temperatures in excess of

approximately 1200°C. If the segregation of the alumina and silica is too pronounced the necessary amount of diffusion cannot take place and the alumina and silica will independently crystallise to give quartz and corundum.

The general direction that has been taken has been to produce relatively homogenous powders and then to densify using hot pressing techniques at high temperatures, 1350°C or above. The direction that was taken in this study was to establish whether a mullite glass could be made and then transformed to mullite as essentially the only crystalline phase.

6.2 Synthesis

The general sol-gel routes that are used involve the use of various amounts of water to initiate the hydrolysis and subsequent polycondensation reactions of the precursors. This approach is complicated when a multicomponent system is being studied, as the reactivity of the precursors to water are unlikely to be similar. Modifications in the synthesis route must then be made in order to minimise the effect of one precursor in preference to the others. If this should happen the fact that water liberating condensation reactions will dominate any alcohol liberating reactions leads to the formation of regions of inhomogeneity, effectively a phase separation phenomenon. The minimisation of the preferential hydrolysis problem is therefore the most important consideration in the formation of homogeneous sols.

It was decided to attempt to develop a pathway to yield a material of the maximum level of homogeneity possible. In the pursuit of this aim the amount of water that was deliberately added to the system was kept to a minimum level, quickly getting to the stage where the atmosphere was providing the water needed for hydrolysis. This approach allows the fabrication of a powder that can be converted mainly to mullite at 980°C. From both a scientific and technological point of view this is unsatisfactory, the amount of water that enters the system is not known and so the strict replication of the procedure cannot be precisely carried out. The extension of this limited water approach to deliberately excluding any water from any external source allows a more detailed synthesis method to be described. When the solution had been stirred for a given period of time an aliquote could be decanted and dried leaving an alcogel.

Once the fabrication route had been developed a method to characterise the materials needed to be established. The most stable phase at the stoichiometry of mullite is crystalline mullite, it follows that the most stable amorphous, or highly disordered, structure is that which is most closely resembles mullite. Hence on crystallisation mullite will be the dominant, if not the only, crystalline phase yielded by such an amorphous structure. Based on this premise, the ratio of the amount of mullite and spinel, the only other crystalline phase observed at 980°C, was arbitrarily defined as the homogeneity coefficient. This coefficient showed a regular variation with the amount of stirring the base solution had undergone. According to this parameter the material started off as being inhomogeneous, that is insufficient stirring had been carried out to give optimum mixing of the precursors. The homogeneity then rises to a maximum, where mullite as the only phase crystallises out, this indicates random and intimate mixing of the alumina and silica polyhedra. The homogeneity then decreases on further stirring, indicating that some segregation process is occurring.

At a very early stage in the reaction the alkoxides, particularly the aluminium alkoxides would still have a relatively high degree of association, the solution would still be at this time inhomogeneous. The more the solution is agitated the more homogeneous the alkoxide mix is. The number of condensation reactions that are occurring also increases with time. Thus the oligomeric species that are being formed get larger, or longer if we assume that they grow linearly. The work done on the mechanisms of condensation of silicon alkoxides (see chapter 1) suggests that low water concentration leads to linear polymeric species. This is the basis of the assumption of linearly growing polymers. Since aluminium alkoxides are more reactive than their silicon counterparts, it may be that they provide the active intermediate species, possibly during a reaction with the solvent alcohol. As the level of homogeneity of the solution increases the more random the condensation reactions, in terms of the species reacting. That is, if the solution is inhomogeneous, and an active aluminium species is formed, it is more likely to react with a passive aluminium species than with a passive silicon species. As the linear polymeric chain grows it reflects the homogeneity of its parent solution, from a homogeneous solution a random polymer would be formed, although more Al-O-Al bonds will be formed than Si-O-Si due to the

composition of the system.

The longer the chain is the more likely that the chain will come into contact with another chain. The aluminium species within the chain are still more reactive than their silicon counterparts. Due to the relative valencies of the aluminum and silicon, there is more steric hindrance around the silicon than the aluminium. Thus it is likely that any cross linking that occurs is between aluminium atoms. The overall homogeneity of the system is therefore decreased as cross linking takes place. This may be the segregation process mentioned earlier.

The general mechanisms is thus, the aluminium alkoxide reacts with the alcohol to give an active species. This active species may then react with a passive alkoxide (aluminium or silicon) or another active species, to give a simple oligomer. The homogeneity of the oligomer will depend on the homogeneity of the solution. As the oligomers get longer the degree of cross-linking increases, this cross-linking is preferentially via aluminium members of the chain, thus decreasing the homogeneity of the system. This is shown schematically in fig. 6.1.

The generally accepted sol-gel reactions for the building up of a network demand that water be present. The fabrication route developed during this study added no water to the alkoxide/alcohol solution, yet sols were built up and occasionally a gel was allowed to form. Although the alkoxides themselves were not of ultra high purity and the extreme conditions required for zero water contamination were not used, it must be remembered that sol-gel is a water consuming process. The regular and reproducible variation in the homogeneity suggests that condensation reactions were taking place. The reactions observed here may be a usual part of sol-gel, their effect may be swamped by the water dominated reactions. Alternatively these reactions may be limited to systems of very low water content, or to specific mixtures of alkoxides and alcohols.

6.3 The 980°C transformation

Central to any study of mullite and related materials is the presence of the 980°C exotherm. The detailed nature of the transformations that occur at this temperature, and more importantly the underlying causes for the transformations have been the subject of a

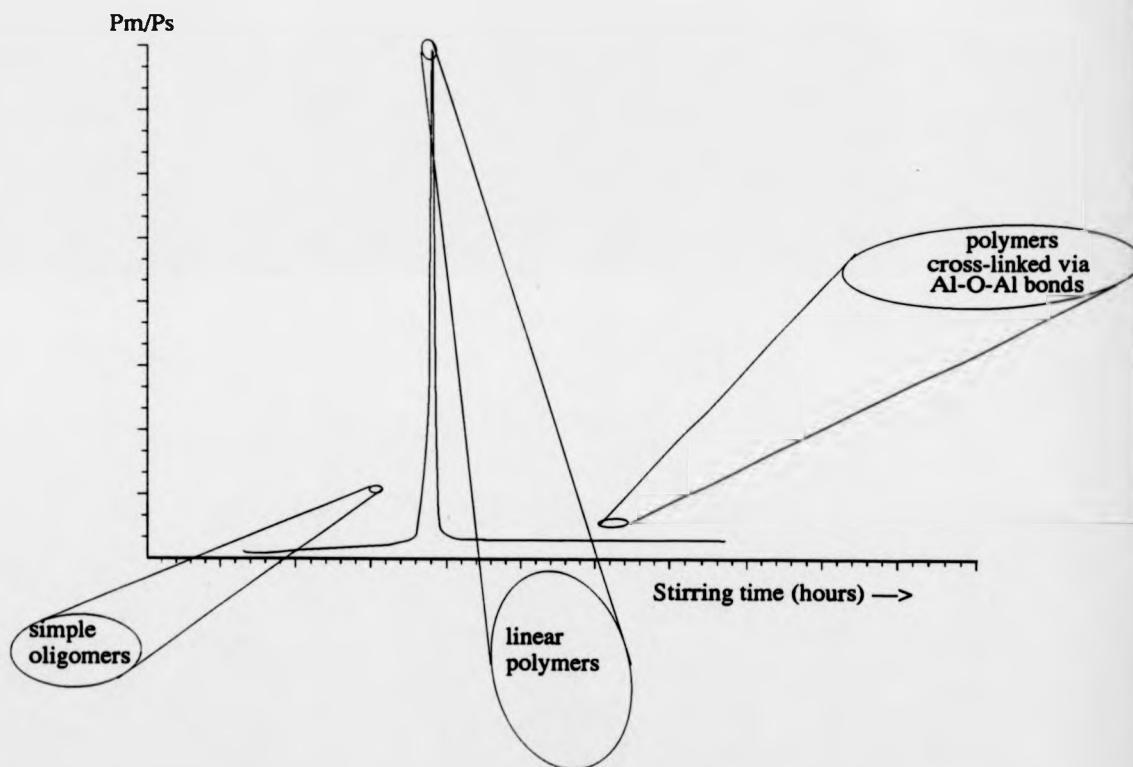


Figure 6.1) Schematic representation of the species proposed at various stirring times.

great deal of discussion for a long time. Any aluminosilicate that is heated to 980°C will undergo the transformation. The phases that result from the transformation depend on the detailed structure of the material, both in terms of the compositional homogeneity and the structural arrangement of the coordination polyhedra. The study that has been carried out has led to the postulation of a crystallisation mechanism based on these considerations. The general observations that have been made are, the more aluminium that is present in the xerogel in five fold coordination the more mullite is produced on heating to the completion of the 980°C exotherm. Conversely, the more octahedral aluminium in the xerogel the more spinel is yielded on heating to above 980°C. This allows us to approximately equate the amount of pentacoordinated aluminium with the homogeneity, with the formation of only mullite as the criterion of optimum homogeneity. Relatively homogeneous xerogels stay x-ray amorphous after low temperature heat treatments for longer than comparatively inhomogeneous xerogels. As the level of homogeneity of the xerogel increases, less spinel is yielded after these low temperature treatments. This indicates that the more homogeneous structures are more stable. These results suggest that we may assume the coprecipitated gel model of Okada and Ōtsuka [82] can be used to describe the overall structure of the materials produced. The regions of inhomogeneity are alumina rich, and these are surrounded by silica rich regions. In the silica rich regions the aluminium occupies tetrahedrally coordinated sites, whilst occupying octahedral sites in the alumina rich regions. As the level of homogeneity increases, so the volume of the inhomogeneities decreases, but the interfacial surface area between them and the silica rich matrix becomes more important. If we assume that the pentacoordinated aluminium exists at this interface, it would be expected that the amount of this polyhedron increases with the increasing homogeneity of the material. This is consistent with the results obtained.

The alumina rich regions are initially x-ray amorphous in the xerogel, the larger the inhomogeneities are however, the more easily they would be expected to crystallise to an alumina polymorph (possibly with some silica substitution). Spinel is the phase that is observed in an inhomogeneous material, after a low temperature heat treatment that does not cause crystallisation in more homogeneous materials.

The pentacoordinated aluminium is metastable and at 980°C dissociates to

tetrahedral and octahedral aluminium. Thus any material that contains this phase will exhibit an exotherm at 980°C. This rearrangement may then initiate crystallisation in the regions around the original polyhedron. The alumina rich regions being metastable themselves would be expected to crystallise to an alumina at their centres and an alumina rich mullite at their boundaries. As the homogeneity increases, the amount of mullite that is yielded would be expected to increase. At the level of optimum homogeneity, where Al-O-Al bonds must exist due to the stoichiometry of the system, it may be expected that only mullite is yielded at 980°C. The mullite should not be alumina rich but of the stoichiometric version.

If, however, the material is heated up very slowly, or subjected to a long time, low temperature heating schedule, the devitrification of the alumina rich regions will occur. This crystallisation may consume the pentacoordinated aluminium before 980°C and so no exotherm is seen at this temperature. Heating programmes of this nature will also favour the ultimate formation of stoichiometric, orthorhombic mullite, as the long soaking times will allow diffusion to occur. Thus compositional irregularities will be smoothed out, especially if they cover relatively small distances initially, as in the case of homogenous materials.

6.4 Conclusions

A method of producing xerogels that crystallise to yield various amounts of mullite and spinel has been established. The synthesis route that has been developed is novel in that no water is deliberately added or, within reason, allowed to contaminate the system. Regular and reproducible variations in the measured homogeneity of the materials produced occur. That mullite is produced indicates that Al-O-Si bonds are being formed, this is evidence for condensation reactions taking place. The nature of these chemical reactions are, as yet, unidentified. The reactions may be speculated on as being always present in sol-gel reactions but usually their effects are swamped by the hydrolysis driven reactions, or that they only occur under special conditions.

A mechanism for the 980°C exotherm has been described. Pentacoordinate aluminium, present at the interface between alumina-rich inhomogeneities and the silica

rich matrix, undergoes a rapid transformation to four- and six-coordinated aluminium. This transformation causes a rearrangement at the interface of the coordination polyhedra of aluminium and silicon. The result of this transformation is alumina-rich mullite at the interface, while within the inhomogeneities this transformation catalyses the crystallisation of spinel. The size of the inhomogeneities determines the major crystalline phase. As the inhomogeneities decrease in volume, the relative importance of the interface increases and the amount of mullite yielded on completion of the exotherm increases.

Low temperature heating of the xerogel causes the inhomogeneities to devitrify, this rearrangement consumes the pentacoordinated aluminium, the more homogeneous the xerogel the higher the temperature, or the longer the soaking time needed, to cause devitrification. The initial level of homogeneity of the xerogel also determines the phases yielded with low temperature treatment.

On high temperature heating of the material (post exotherm) the alumina rich mullite produced at the exotherm reacts with the silica rich matrix to yield stoichiometric orthorhombic mullite. Any residual spinel transforms to corundum.

The amount of densification of the material that takes place at temperatures below 980°C is too little to allow the production of C.M.C articles when processed in the usual manner, i.e hot pressing or sintering. The fabrication of a fully dense article of mullite glass therefore can not be envisaged with the current technology. The crystallisation temperature is an inherent function of the material, if the homogeneity is high the material will not flow viscously before it crystallises because the mullite xerogel has not passed the glass transition point. If the homogeneity is low the silica rich regions will flow, but the alumina rich regions will crystallise at low temperatures. Thus the fabrication of a mullite glass matrix incorporating fibres to achieve a fully dense article is not a viable proposition currently.

6.5 Future Work

In order to build upon this work and to deepen the understanding of sol-gel systems, particularly aluminosilicates with very little water there are several directions which may prove fruitful. During the synthesis of the materials, the variation of the homogeneity

coefficient with the length of time of stirring could be used as the experimental parameter against which changes in fabrication procedure and technique could be estimated. The changes to the synthesis method that should be carried out are; to use different alkoxides of aluminium and silicon, to vary the concentration of the solutions made, to change the alcohol in which the solution is made. These changes will allow a broad map to be defined with the nature of the alcohol, as solvent and also as a ligand, being central to the investigation. The effect of alcohol chain length and steric hindrance should become clearer from this phenomenological study.

The absolute amount of water in the "water-free" synthesis needs to be estimated before any quantitative work is carried out. Then, the effect of controlled amounts of water on the homogeneity variation needs to be carried. This will show whether there is a threshold for water concentration at which the reactions that are occurring are swamped by hydrolysis reactions.

In order to throw some light on the condensation reactions that are occurring, analytical chemical methods should be used to establish what intermediates and reaction by products are formed. These should be closely monitored particularly during the early stages of the reaction. To compliment these techniques ^{29}Si NMR should be used to observe the early species that are formed.

The proposed mechanism for the crystallisation sequence needs to be tested, this could best be done by directly observing the coordination polyhedra of aluminium by NMR whilst heating the material to the exotherm temperature. Prior heat treatment to partially remove the pentacoordinated aluminium should also be carried out. The effect of the removal of this type of aluminium on the exotherm should be noted. Whether the subsequent crystallisation of mullite and/or spinel occurs after partial removal of the pentacoordinated aluminium should also be noted. Apart from the direct observation of the disproportionation, the other transformation studies can be carried out in a more conventional sense.

Other methods of achieving dense articles should be attempted, aerogel technology especially seems promising. This route may allow more dense materials to be produced than more conventional routes or it may allow the production of useful mullite aerogels.

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